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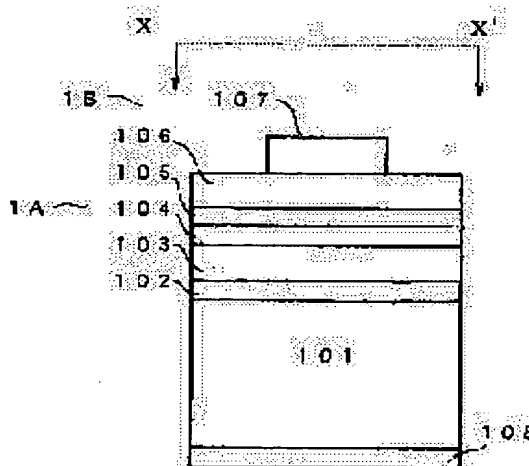
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(54) BORON PHOSPHIDE BASE SEMICONDUCTOR LAYER, METHOD FOR MANUFACTURING THE SAME, AND BORON PHOSPHIDE BASE SEMICONDUCTOR ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for forming a boron phosphide buffer layer which readily and stably provides a continuous boron phosphide base crystal layer on a crystal substrate with unified crystal orientation.

SOLUTION: The boron phosphide buffer layer is formed by a first process for growing a film, whose main constituent is boron, by chemical vapor deposition, while making a boron source flow to the surface of the crystal substrate whose temperature is maintained at a first temperature T1 (where $250^{\circ}\text{C} \leq T1 \leq 750^{\circ}\text{C}$), and a second process for making phosphorus infiltrate the film whose main constituent is boron at a second temperature T2 (wherein $T1 \leq T2 \leq 1,200^{\circ}\text{C}$) and under an atmosphere containing a phosphorus source.



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CLAIMS

[Claim(s)]

[Claim 1] By the vapor growth which makes the compound containing boron (B) the source of boron, and makes the compound containing Lynn (P) the source of Lynn In the manufacture approach of the Lynn-ized boron system semi-conductor layer which carries out sequential formation of the buffer coat (Lynn-ized boron buffer coat) which consists of Lynn-ized boron on the front face of a crystal substrate, and the Lynn-ized boron system crystal layer which uses boron and Lynn as a configuration element The 1st process to which the front face of a crystal substrate is made to carry out vapor growth of the coat which the source of boron is circulated on the front face of the crystal substrate held at the 1st temperature T1 (however, 250 degree-C<=T1 <=750 degree C), and makes boron a subject, The temperature of a crystal substrate then, within an ambient atmosphere including the source of Lynn as the 2nd temperature T2 (however, T1 <=T2 <=1200 degree C) The manufacture approach of the Lynn-ized boron system semi-conductor layer characterized by forming the Lynn-ized boron buffer coat on the front face of a crystal substrate via the 2nd process which makes Lynn permeate the coat which makes said boron a subject.

[Claim 2] The manufacture approach of the Lynn-ized boron system semi-conductor layer according to claim 1 characterized by including the 3rd process which maintains the temperature of a crystal substrate 2nd more than temperature T2, and heat-treats to the Lynn-ized boron buffer coat within the ambient atmosphere which includes the source of Lynn after the 2nd process.

[Claim 3] The manufacture approach of the Lynn-ized boron system semi-conductor layer according to claim 2 characterized by circulating the both sides of the source of boron, and the source of Lynn to coincidence, and including the 4th process which carries out vapor growth of the Lynn-ized boron system crystal layer on the Lynn-ized boron buffer coat.

[Claim 4] The manufacture approach of the Lynn-ized boron system semi-conductor layer according to claim 3 characterized by performing the coat which makes boron a subject for the 2nd, 3rd, and 4th process on the front face of a crystal substrate in the 1st process with the same vapor growth equipment as having carried out vapor growth.

[Claim 5] The manufacture approach of the Lynn-ized boron system semi-conductor layer according to claim 4 characterized by starting supply of the source of Lynn to an ambient atmosphere, and starting the 2nd process at the same time it stops circulation of the source of boron to the front face of a crystal substrate and terminates the 1st process.

[Claim 6] The manufacture approach of the Lynn-ized boron system semi-conductor layer given in claim 1 to which thickness of the coat which makes boron a subject is characterized by 1nm or more being 100nm or less thru/or any 1 term of 5.

[Claim 7] The manufacture approach of the Lynn-ized boron system semi-conductor layer given in claim 1 characterized by performing the 2nd process in the ambient atmosphere which makes the rate of a volume ratio of the source of Lynn 3% or more thru/or any 1 term of 6.

[Claim 8] The manufacture approach of the Lynn-ized boron system semi-conductor layer given in claim 2 characterized by heat-treating the Lynn-ized boron buffer coat for [for / 5 minutes / -] 40 minutes at the 3rd process thru/or any 1 term of 5.

[Claim 9] The manufacture approach of the Lynn-ized boron system semi-conductor layer given in claim 1 characterized by using a silicon (Si) single crystal as a crystal substrate thru/or any 1 term of 8.

[Claim 10] The Lynn-ized boron system semi-conductor layer manufactured by the manufacture approach of the Lynn-ized boron system semi-conductor layer a publication in claim 1 thru/or any 1 term of 9.

[Claim 11] The Lynn-ized boron system semiconductor device which comes to have the Lynn-ized boron system semi-conductor layer according to claim 10.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] the manufacture approach of the Lynn-ized boron system semi-conductor layer which carries out sequential formation of the buffer coat (Lynn-ized boron buffer coat) to which this invention consists of Lynn-ized boron on the front face of a crystal substrate, and the Lynn-ized boron system crystal layer which uses boron and Lynn as a configuration element — starting — especially, drawing — it is related with the technique for carrying out vapor growth of the Lynn-ized boron system crystal layer which has orientation bearing [one].

[0002]

[Description of the Prior Art] Conventionally, since various semiconductor devices are constituted, the Lynn-ized boron system semi-conductor layer which uses boron (B) and Lynn (P) as a configuration element is used. For example, the semi-conductor layer which consists of Lynn-ized boron (BP) of a monomer typical as a Lynn-ized boron system semi-conductor is used for constituting n form base (base) layer of a npn mold hetero-bipolar transistor (HBT) (J. refer to Electrochem.Soc., 125 (4) and (1978), and 633 – 637 pages). Moreover, it is in a blue laser diode (LD), and is used as a contact (contact) layer for forming the low ohmic (Ohmic) electrode of contact resistance (refer to JP,10-242567,A). Moreover, it is used as a buffer coat for constituting the light emitting diode (LED) which brings about luminescence of short wavelength, such as near-ultraviolet or blue, (refer to U.S. Pat. No. 6,069,021 number).

[0003] The Lynn-ized boron system semi-conductor layer for constituting a semiconductor device is conventionally formed by the vapor growth means like the above. the halogen (halogen) vapor growth (“a Japanese crystal growth society magazine” —) which uses boron trichloride (BCl₃) and a phosphorus trichloride (PCl₃) as a start raw material from the former at a vapor growth means the hydride (hydride) vapor growth (J. — Crystal Growth — 24/25 (1974)) which uses Vol.24, to refer to the No. 2 (1997) or 150 page, borane (BH₃) or diboron hexahydride (B-2 H₆), a phosphine (PH₃), etc. as a raw material refer to the 193-196 page and a molecular beam epitaxy (J. — Solid State Chem. and 133 (1997) —) refer to the 269-272 page and organic metal chemical gaseous-phase deposition (MOCVD) — law (Inst.Phys.Conf.Ser. and No.129 (refer to IOP Publishing Ltd. (UK, 1993) and 157-162 pages) can be illustrated.)

[0004] it faces carrying out vapor growth of the Lynn-ized boron system semi-conductor layer, and it appears in a substrate to use the single crystal of a semiconductor material chiefly. Before, single crystals, such as a silicon (Si) single crystal (silicon) (refer to above-mentioned **J.Electrochem.Soc., 125 (1978), and ** U.S. Pat. No. 6,069,021 number), silicon carbide (SiC) (refer to JP,10-242569,A), gallium phosphide (GaP) (refer to JP,10-242568,A), and gallium nitride (GaN) (refer to JP,10-247745,A), are used as a practical substrate. However, for example, the lattice constant of a silicon single crystal is 5.431Å, and it of BP of a sphalerite mold is 4.538Å (refer to the Teramoto ****, “semiconductor device introduction” (March 30, 1995, Baifukan Issue First edition), and 28 pages). therefore, whenever [lattice mismatch] size-came with about 16.5%, and is boiled and attained (refer to the Shono Katsufusa work, “semiconductor technology (above)” (June 25, 1992, University of Tokyo Press issue 9 **), and 97 – 98 pages).

[0005]

[Problem(s) to be Solved by the Invention] Thus, on the crystal substrate which makes whenever [lattice mismatch] size, the Lynn-ized boron system semi-conductor layer has Mr. Volmer-Weber's growth format, and causes island-shape growth (refer to the volume Japan Society of Applied Physics thin films and for surface physics subcommittees, a “thin film production handbook” (March 25, 1991, the 1st ** of the KYORITSU SHUPPAN Co., Ltd. issue first edition), and 59 pages). In island-shape growth, orientation of each growth island is not necessarily uniformly carried out along with fixed crystal orientation. For this reason, the Lynn-ized boron system semi-conductor layer which progresses considering a growth island as a growth nucleus also has a fault used as the heterogeneous thing which consists of crystallines of a disorderly stacking tendency. Or since the cause of the island-shape Stranski-Krastanov format-like (refer to above-mentioned “thin film production handbook” and 59 pages) growth is carried out, trouble has been caused to that the Lynn-ized boron system semi-conductor layer with the continuity which is excellent in surface surface smoothness may be stabilized.

[0006] If there is a vapor growth means effective in offering the Lynn-ized boron system semi-conductor layer which comes to have the crystalline of a uniform stacking tendency, using it, a normal pn junction property can be manifested itself and LED with low forward voltage (the so-called Vf) and LD with low threshold voltage

(the so-called Vth) can be offered simple. Especially in this invention, the formation approach of the Lynn-ized boron buffer coat for hanging down the Lynn-ized boron system crystal layer with the continuity which has uniform crystal-face bearing on the crystal substrate which makes whenever [lattice mismatch] size, even if stabilized simple is offered. Moreover, the Lynn-ized boron system semiconductor device constituted in the buffer coat list using the Lynn-ized boron system crystal layer is offered.

[0007]

[Means for Solving the Problem] By namely, the vapor growth which this invention makes the compound containing (1) boron (B) the source of boron, and makes the compound containing Lynn (P) the source of Lynn In the manufacture approach of the Lynn-ized boron system semi-conductor layer which carries out sequential formation of the buffer coat (Lynn-ized boron buffer coat) which consists of Lynn-ized boron on the front face of a crystal substrate, and the Lynn-ized boron system crystal layer which uses boron and Lynn as a configuration element The 1st process to which the front face of a crystal substrate is made to carry out vapor growth of the coat which the source of boron is circulated on the front face of the crystal substrate held at the 1st temperature T1 (however, $250\text{ degree-C} \leq T1 \leq 750\text{ degree C}$), and makes boron a subject, The temperature of a crystal substrate then, within an ambient atmosphere including the source of Lynn as the 2nd temperature T2 (however, $T1 \leq T2 \leq 1200\text{ degree C}$) The manufacture approach of the Lynn-ized boron system semi-conductor layer characterized by forming the Lynn-ized boron buffer coat on the front face of a crystal substrate via the 2nd process which makes Lynn permeate the coat which makes said boron a subject.

(2) The manufacture approach of the Lynn-ized boron system semi-conductor layer given in the above (1) characterized by including the 3rd process which maintains the temperature of a crystal substrate 2nd more than temperature T2, and heat-treats to the Lynn-ized boron buffer coat within the ambient atmosphere which includes the source of Lynn after the 2nd process.

(3) The manufacture approach of the Lynn-ized boron system semi-conductor layer given in the above (2) characterized by circulating the both sides of the source of boron, and the source of Lynn to coincidence, and including the 4th process which carries out vapor growth of the Lynn-ized boron system crystal layer on the Lynn-ized boron buffer coat.

(4) The manufacture approach of the Lynn-ized boron system semi-conductor layer given in the above (3) characterized by performing the coat which makes boron a subject for the 2nd, 3rd, and 4th process on the front face of a crystal substrate in the 1st process with the same vapor growth equipment as having carried out vapor growth.

(5) The manufacture approach of the Lynn-ized boron system semi-conductor layer given in the above (4) characterized by starting supply of the source of Lynn to an ambient atmosphere, and starting the 2nd process at the same time it stops circulation of the source of boron to the front face of a crystal substrate and terminates the 1st process.

(6) The above (1) to which thickness of the coat which makes boron a subject is characterized by 1nm or more being 100nm or less thru/or the manufacture approach of the Lynn-ized boron system semi-conductor layer given in any 1 term of (5).

(7) The above (1) characterized by performing the 2nd process in the ambient atmosphere which makes the rate of a volume ratio of the source of Lynn 3% or more thru/or the manufacture approach of the Lynn-ized boron system semi-conductor layer given in any 1 term of (6).

(8) The above (2) characterized by heat-treating the Lynn-ized boron buffer coat for [for / 5 minutes / -] 40 minutes at the 3rd process thru/or the manufacture approach of the Lynn-ized boron system semi-conductor layer given in any 1 term of (5).

(9) The above (1) characterized by using a silicon (Si) single crystal as a crystal substrate thru/or the manufacture approach of the Lynn-ized boron system semi-conductor layer given in any 1 term of (8).

It comes out.

[0008] Moreover, this invention is the Lynn-ized boron system semi-conductor layer manufactured by the manufacture approach of the Lynn-ized boron system semi-conductor layer (10) above (1) thru/or given in any 1 term of (9).

(11) The Lynn-ized boron system semiconductor device which comes to prepare the Lynn-ized boron system semi-conductor layer of a publication for the above (10).

It comes out.

[0009]

[Embodiment of the Invention] In the manufacture approach of the Lynn-ized boron system semi-conductor layer of this invention, the 1st process is a process for forming in the front face of a crystal substrate the coat which is made to carry out the pyrolysis of the source of boron which consists of a compound containing boron, and makes boron a subject. As a source of boron, organic boron compounds, such as boron hydrides, such as halogenation boron compounds, such as boron trichloride (BCl₃) and three bromine chlorides (BBr₃), borane (BH₃), or diboron hexahydride (B₂H₆), or boron triethyl (C₂H₅)₃B, can be illustrated. It supplies towards the front face of the crystal substrate which had these sources of boron heated, and the coat which was made to put the boron emitted by the pyrolysis of the source of boron on a crystal substrate, and made boron the subject is formed. The elements or decomposition products other than the boron which was based on the pyrolysis of the source of boron and was generated may be included in a coat. For example, on the coat

formed as a source of boron, carbon (C) or hydrogen (H) may contain $3(C_2H_5)_2B$ in addition to boron. The coat which makes boron a subject is a coat which makes the weight content of boron 80% or more. It is suitable for formation of the coat which makes boron a subject to hold the temperature of a crystal substrate at 250 degrees C or more. For it being stabilized and forming the coat which the pyrolysis of the source of boron does not fully advance, but makes boron a subject at the temperature of less than 250 degrees C, it is inconvenient. Moreover, at the elevated temperature exceeding 750 degrees C, condensation of the boron which constitutes a coat takes place notably, and the coat of the shape of a semi-sphere which makes boron a subject causes the condition that it is scattered on the front face of a crystal substrate in island shape. For this reason, difficulty is caused to obtaining the Lynn-ized boron system crystal layer which is continuous at the 4th process which does not come to cover the front face of a crystal substrate with the coat which makes boron a subject to homogeneity, and mentions it later with it to it. That is, it is in the 1st process which forms the coat which makes boron a subject, and the suitable temperature T_1 (degree C) becomes 250 degree- $C \leq T_1 \leq 750$ degree C.

[0010] In the 1st process, although the coat which makes boron a subject can be formed using two or more sorts of sources of boron, it can form a coat for the source of boron individually, then simple, and is convenience. Sources of boron, such as $3B$ which is a liquid at a room temperature (C_2H_5), can be supplied in the vapor growth equipment for making it accompany to gases for foaming (bubbling), such as hydrogen, and forming a coat. For example, the thickness of a coat will be increased, if the flow rate of the gas for foaming in the source of boron is made to increase when supplying $3(C_2H_5)_2B$ maintained to constant temperature in fixed time amount and vapor growth equipment and forming a coat. (C_2H_5) If it is made to mix with conveyance (carrier) gas and the gas which accompanies the steam of sources of boron, such as $3B$, is circulated further, it is stabilized without an intermission by the interior of vapor growth equipment, and the source of boron can be supplied. Simple substance gas, such as an argon (Ar), can be used for a conveyance gas at hydrogen (H_2) and a nitrogen (N_2) list. As for the thickness of a coat, it is desirable to be referred to as 100nm or less by 1nm or more. In a less than 1nm **** thin film, the coat which makes boron a subject serves as trouble obtaining the Lynn-ized boron system crystal layer which does not come to cover the front face of a crystal substrate uniformly enough, and covers the front face of a crystal substrate with the 4th process uniformly. Moreover, in the thick film with which the thickness of a coat exceeds 100nm, since it is inferior to surface surface smoothness, difficulty is caused to obtaining the Lynn-ized boron system crystal layer which makes a front face flat and makes thickness uniform in the 4th process. Moreover, if thickness is used as the thick film further exceeding about 200nm, it may produce un-arranging [for which the coat which makes boron a subject exfoliates] from a crystal substrate. The still more suitable thickness of the coat which makes boron a subject is about 5nm - about 50nm generally.

[0011] The 2nd process is a process for making the coat which heat the coat which makes a subject the boron formed on the front face of a crystal substrate at the 1st process within an ambient atmosphere including the source of Lynn, and Lynn is made to permeate the interior of a coat, and makes boron a subject convert into the buffer coat which consists of Lynn-ized boron. As a source of Lynn, the Lynn hydrides, such as halogenation phosphorus compounds, such as a phosphorus trichloride (PCl_3) and phosphorus tribromide (PBr_3), and a phosphine (PH_3), or an organic phosphorous compound can be illustrated. The phosphorus compounds containing oxygen (O) exert the oxidation on the boron which constitutes a coat actively, or Lynn which permeated the coat, and since they bring about the sludge which consists of an oxide, they cannot change with the desirable source of Lynn. Although only the source of Lynn can be circulated and an ambient atmosphere can also be constituted, if the source of Lynn is circulated with the above-mentioned carrier gas, the ambient atmosphere in which the concentration of the source of Lynn was adjusted can be created, for example. For example, the ambient atmosphere which circulates the mixed gas of the hydrogen of PH_3 and carrier gas inside the vapor growth equipment which formed the coat in the 1st process, and includes the source of Lynn inside is constituted. In this case, if the temperature which performs the 2nd process is taken into consideration, when the rate of a volume ratio of the source of Lynn in the mixed gas of an ambient atmosphere will be made into 3% or more, it is made to permeate efficiently the coat which makes boron a subject in Lynn. the amount of Lynn which exists in a coat — for example, secondary ion mass analysis (SIMS) — a quantum can be carried out by elemental-analysis methods, such as law, and Auger electron spectroscopy (AES), an electron ray probe (probe) X-ray analysis.

[0012] From the temperature (the 1st temperature T_1) of the crystal substrate in the 1st process, the temperature (the 2nd temperature T_2) of the crystal substrate in the 2nd process is an elevated temperature, and is made into the temperature of 1200 degrees C or less. At the elevated temperature exceeding 1200 degrees C, generating of the Lynn-ized boron polymer of the $B_{13}P_2$ grade of the rhombohedron crystal structure is caused (J. refer to Am.Ceramic Soc., 47 (1) and (1964), and 44 - 46 pages), and it becomes inconvenient for obtaining the crystalline equal Lynn-ized boron system crystal layer as the upper layer, for example. It becomes impossible to, emit efficiently Lynn which makes boron permeate the coat which becomes as a subject since the pyrolysis of the source of Lynn does not fully advance at the temperature below T_1 (250 degree- $C \leq T_1 \leq 750$ degree C) on the other hand, and is inconvenient. Therefore, the range of the 2nd temperature T_2 (degree C) which becomes suitable at the 2nd process is $T_1 \leq T_2 \leq 1200$ degree C. When the halogenation phosphorus compounds of PCl_3 grade are used as a source of Lynn, it is based on the halogenide generated in a pyrolysis, and the coat which becomes considering boron as a subject may be etched (etching).

Since etching becomes remarkable so that it is an elevated temperature, in case halogenation phosphorus compounds are made into the source of Lynn, as for the 2nd temperature in the 2nd process, it is desirable to set it as low temperature comparatively within the limits of [suitable] the above. That is, it is desirable to consider as 950 degrees C or less in general. When the etching based on the source of Lynn does not occur, the thickness of the Lynn-ized boron layer obtained after ending the 2nd process serves as the thickness of a coat and the abbreviation EQC which make a subject the boron formed at the 1st process.

[0013] As a good example of the 1st operation gestalt of this invention, as the 1st process, boron triethyl (C_2H_5) (3B) is used for the source of boron, and the 1st temperature T1 is made into 450 degrees C. Within MOCVD growth equipment Vapor growth of the coat which consists of boron which sets thickness to about 20nm on the front face of the silicon single crystal substrate ([111]-silicon single crystal substrate) which has the {111} crystal faces is carried out. After that as the 2nd process The technique of forming the Lynn-ized boron layer via the process which makes Lynn permeate the coat which consists of the above-mentioned boron, carrying out the temperature up of the temperature of a substrate to 1050 degrees C which is the 2nd temperature (= T2) from 450 degrees C in the hydrogen ambient atmosphere which makes it volume percentage and contains 6% of phosphine (PH_3) can be mentioned. The Lynn-ized boron layer formed through the 1st and 2nd processes can act as a buffer coat effective in bringing about the upper layer which eases a lattice mismatch with a crystal substrate and is excellent in crystallinity. This buffer coat acts as a buffer coat which can also hang down the Lynn-ized boron system crystal layer which excelled further the low-temperature buffer coat (refer to the above-mentioned U.S. Pat. No. 6,069,021 number) to which the front face of a crystal substrate was made to supply collectively and carry out vapor growth of the conventional source of boron and the conventional source of Lynn in surface surface smoothness. Moreover, the operation which brings about the Lynn-ized boron system crystal layer which consists of the crystal face of uniform crystal orientation as the upper layer is demonstrated.

[0014] After forming the Lynn-ized boron buffer coat which acts effectively as a buffer coat via the 1st and 2nd above-mentioned processes, moreover, it can make with the buffer coat with the uniform Lynn presentation of this Lynn-ized boron buffer coat to which the stacking tendency was equal by heat-treating within an ambient atmosphere including the source of Lynn further (anneal). At low temperature, in order for the pyrolysis of the source of Lynn not to fully advance and to attract generating of the Lynn-ized boron polymer at an elevated temperature, it is suitable to carry out heat treatment temperature to more than the 2nd temperature T2 (however, $T_1 \leq T_2 \leq 1200$ degree C). The ambient atmosphere needs to contain the source of Lynn of the partial pressure exceeding the pressure of the Lynn molecule dissociated from Lynn-ized boron at least in the temperature which performs the heat treatment. The dissociation pressure (P; unit hPa) of Lynn-ized boron sets temperature to T (unit: K), and it is supposed that it is asked from the relational expression (1) of degree account (J. refer to Am.Chem.Soc., 82 (1960), and 1330-1332 pages).

$\log P = -(13.7 \times 10^3 / T) + 10.2$ Relational expression (1)

The effectiveness of equalization of the presentation which depends on heat treatment, or uniformization of a stacking tendency may be attained also about the Lynn-ized boron of a presentation out of balance to the stoichiometric which does not balance in equivalent.

[0015] As a good example of the 2nd operation gestalt of this invention, it goes through the 1st and 2nd processes, and the technique of performing heat treatment over for 15 minutes in the ambient atmosphere which consists of mixed gas of PH_3 and Ar which makes it volume percentage and contains 10% of PH_3 at the same 950 degrees C as the 2nd temperature of the 2nd process can be mentioned in the 3rd process to the buffer coat which consists of formed Lynn-ized boron. The effectiveness which depends on heat treatment depends on carrying out heat treatment temperature to beyond the 2nd [of the 2nd process] temperature, and can be discovered notably. However, heat treatment in the elevated temperature exceeding 1200 degrees C is not desirable in order to bring about the heterogeneous Lynn-ized boron buffer coat which causes generating of the polymer of B13P2 grade, and is different in a crystal mold despite a join office. As heat treatment time amount of the 3rd process, it is suitable to consider as for [for / about 5 minutes / -] 40 minutes. Heat treatment concerning the 3rd process is not limited to a means to hold [fixed time amount] to fixed temperature. For example, there is also a temperature up or the technique of heat-treating to temperature more nearly another than a certain temperature T2, lowering the temperature. After ending the 2nd process as another example of the 2nd operation gestalt of this invention, using the 2nd temperature as 900 degrees C, in the ambient atmosphere which consists of mixed gas of PH_3 and N_2 which makes it volume percentage and contains 8% of PH_3 , the temperature up of the temperature of the Lynn-ized boron buffer coat is carried out at the rate of 20 degrees C/m to 1100 degrees C, and the technique of heat-treating for 10 minutes can be mentioned. The temperature up in a rapid rate or a temperature fall will introduce a thermal strain into a buffer coat on the contrary. On the contrary, the temperature up in a slow rate or a temperature fall increases the opportunity of volatilization of Lynn from a buffer coat to **, and promotes disorderly-ization of the front face of the buffer coat based on deviation of Lynn. The temperature up or temperature fall rate which becomes suitable to eliminate such a problem is in the range of about 50 degrees C per minute from about 10 degrees C per minute generally.

[0016] Like the above, the Lynn-ized boron layer formed via the 1st and 2nd processes can be effectively used as a buffer coat which eases a lattice mismatch with a crystal substrate. Therefore, on this buffer coat, the Lynn-ized boron system crystal layer which makes crystallinity with few crystal defects good is grown up.

for example, $\text{B}_{1-\alpha}\text{Al}_{\alpha}\text{Ga}_{1-\beta}\text{In}_{\beta}\text{P}_{1-\gamma}\text{As}_{\gamma}$ ($0 < \alpha \leq 1$, $0 \leq \beta < 1$, $0 \leq \gamma < 1$, $0 < \alpha + \beta + \gamma \leq 1$, $0 \leq \delta < 1$) which includes boron and Lynn as a configuration element with the Lynn-ized boron system crystal layer — moreover — for example It is $\text{B}_{1-\alpha}\text{Al}_{\alpha}\text{Ga}_{1-\beta}\text{In}_{\beta}\text{P}_{1-\gamma}\text{N}_{\gamma}$ ($0 < \alpha \leq 1$, $0 \leq \beta < 1$, $0 \leq \gamma < 1$, $0 < \alpha + \beta + \gamma \leq 1$, $0 \leq \delta < 1$). In order to use as stratum functionale for constituting a semiconductor device, it is suitable for these Lynn-ized boron system crystal layers to stoichiometric that balance can be taken. Therefore, unlike the case where vapor growth of the Lynn-ized boron buffer coat is carried out in the 1st process, the Lynn-ized boron system crystal layer circulates to coincidence, and forms the both sides of the source of boron, and the source of Lynn on the Lynn-ized boron buffer coat. while circulating $3(\text{C}_2\text{H}_5)\text{B}$, trimethylgallium $(\text{CH}_3)(3\text{Ga})$, and PH_3 in parallel to a Lynn-ized boron (BP) buffer coat top as the 4th process as an example of the 3rd operation gestalt of this invention — MOCVD — the example to which it depends on law and vapor growth of the $\text{BXGa}_{1-X}\text{P}$ ($0 < X \leq 1$) layer of a indirect transition mold is carried out can be given.

[0017] After suspending supply of the source of boron and terminating formation of the coat which makes boron a subject at the 1st process, the source of Lynn is supplied to an alternative, and if it carries out to advancing the 2nd process succeedingly, in the same vapor growth equipment, vapor growth of the Lynn-ized boron buffer coat will be carried out simple. If it depends on this technique, since it can shift to the 2nd process, without putting the coat which makes boron a subject after ending the 1st process to atmospheric air, it is based on formation of a boron oxide and can prevent that the smooth nature on the front face of a coat is spoiled, for example. Moreover, if the 3rd and 4th processes are carried out with the same vapor growth equipment following on the 2nd process, there is an advantage which can carry out simply the 2nd, 3rd, and 4th processes without an intermission. moreover, the source of boron same at the process from the 1st to the 4th and the source of Lynn — the thing of ***** — the Lynn-ized boron system semi-conductor layer can be formed simple. As a good example of the 4th operation gestalt of this invention, the case where the 1st, 2nd, 3rd, and 4th processes are carried out for diboron hexahydride (B_2H_6) and a phosphine (PH_3) within the same hydride vapor growth equipment as a common raw material can be mentioned.

[0018] Supply of the source of boron which used boron for the formation of a coat made into a subject at the 1st process is suspended, and carrying out a temperature up to the 2nd temperature for the 2nd process, shortly after combining and starting supply of the source of Lynn, the Lynn-ized boron buffer coat which gives the Lynn-ized boron system crystal layer which makes crystal-face bearing uniform can be constituted. The crystal layer which becomes uniform especially from the same crystal face as the crystal face of a crystal substrate front face is obtained. For example, the Lynn-ized boron buffer coat which can also hang down the Lynn-ized boron system crystal layer which becomes uniform from the {111} crystal faces on a {111}-silicon single crystal substrate can be offered. If spacing of the long duration which will exceed for about 1 minute by the time it starts supply of the source of Lynn is prepared after suspending supply of the source of boron used for the 1st process, the Lynn-ized boron buffer coat which sometimes gives the Lynn-ized boron system crystal layer in which the crystal which is different in crystal-face bearing is intermingled may be concluded. This is considered that it originates in generating of the polygon configuration formed when supply of the source of boron is suspended and a coat is left within the ambient atmosphere of only carrier gas for a time, or a spherical boron object. the situation of generating of such a spherical boron object can be grasped in the publication already exhibited (J. — Solid State Chem., 133 (1997), and 314–321 pages — it is — especially — FIG.2 of 316–page printing). While suspending supply of the source of boron of $3(\text{C}_2\text{H}_5)\text{B}$ used at the 1st process as an example of the 5th operation gestalt of this invention, it supplies in the MOCVD vapor growth equipment which used PH_3 at the 1st process, and the technique of starting the 2nd process immediately can be mentioned.

[0019] On the Lynn-ized boron buffer coat formed via the 1st and 2nd processes of this invention, it depends on the 4th process and the Lynn-ized boron system crystal layer which is excellent in crystallinity can be prepared. It becomes what excelled [upper layer / a substrate layer, then / its] the good Lynn-ized boron system crystal layer of this crystallinity in crystallinity. If the good Lynn-ized boron system crystal layer or the good upper layer of these crystallinity is utilized as various stratum functionale, the Lynn-ized boron system semiconductor device which is excellent in a property can be constituted. The case where the pn junction mold Lynn-ized boron system semi-conductor LED is constituted from the epitaxial laminating structure which equipped with each stratum functionale of a publication following (a) – (e) prepared on the silicon single crystal substrate as an example of the 6th operation gestalt of this invention can be mentioned.

(a) After making Lynn permeate the boron coat formed at the 1st process at the 2nd process, Heat-treated at the 3rd process, and depended and formed the source of boron, and the source of Lynn in the vapor growth supplied to coincidence at the 4th process of the Lynn-ized boron buffer coat (b) of making Lynn coming to be distributed over homogeneity. The MOCVD growth equipment used at the 1st thru/or the 4th process is used. for example, p form lower cladding layer (c) which consists of the so-called Lynn-ized boron crystal layer of undoping (undope) which has not added the impurity — The same, same MOCVD growth equipment is used. n form luminous layer (d) which consists of a gallium nitride indium ($\text{GaXIn}_{1-X}\text{N}$:0 $\leq X \leq 1$) which the preceding clause (b) was made to join to the lower cladding layer of a publication, and carried out vapor growth to it — The same, same MOCVD growth equipment is used. the antilashing layer (e) for controlling volatilization of the indium (In) from a luminous layer which consists of Lynn-ized boron of n form by undoping which was made to

join to the luminous layer of the preceding clause (c), and was prepared — The rear face of the conductive silicon single crystal substrate of the epitaxial laminating structure which equipped with each stratum functionale of a publication the up cladding layer pan which consists of Lynn-ized boron of n form by undoping which was made to join to the antilashing layer of the preceding clause (d), and was prepared at above-mentioned (a) – (e), The ohmic electrode which differs in a polarity mutually in contact with the up cladding layer of the outermost layer of this laminating structure can be prepared respectively, and LED can be constituted.

[0020]

[Function] The coat which makes a subject the boron formed at the 1st process of this invention demonstrates the operation which brings about behind the Lynn-ized boron buffer coat which covers the front face of a crystal substrate to homogeneity uniformly, and which is excellent in surface surface smoothness.

[0021] An ambient atmosphere including the source of Lynn in the 2nd process of this invention makes Lynn permeate the coat which makes boron a subject, and has the operation which converts into the Lynn-ized boron buffer coat the coat which makes boron a subject.

[0022]

[Example] (The 1st example) The 1st process and 2nd process of this invention are first explained concretely using the example which forms the Lynn-ized boron layer from the coat of the boron formed on the silicon single crystal substrate.

[0023] In the **** 1 example, the coat which consists of boron as the 1st process was formed using common halogen vapor growth equipment (for example, the Institute of Electronics and Communication Engineers "semi-conductor – transistor study group data / data number SSD74-89 (1975-03) (March 25, 1975) reference) on the front face of a p form {111}-Si single crystal substrate. The temperature of Si single crystal substrate was maintained at 350 degrees C. The coat of boron formed boron trichloride (BCl₃) as a source of boron. After making BCl₃ foam with hydrogen gas, it was supplied to vapor growth equipment. The temperature of BCl₃ was maintained at 0 degree C, and the flow rate of the hydrogen gas for foaming which accompanies the steam was adjusted to 15ml/m (ml). Moreover, the hydrogen gas for conveyance of 8l./m (l) was mixed, and the hydrogen gas for foaming which accompanies the steam of BCl₃ was supplied for 8 minutes in the vapor growth furnace provided to above halogen vapor growth equipment. Supply to the hydrogen carrier gas of the hydrogen gas for foaming which accompanies the steam of BCl₃ was suspended, the 1st process which forms the coat of boron was ended, and the substrate was cooled to the temperature near the room temperature. Then, Si single crystal substrate on which the coat of boron was made to put was taken out from the vapor growth furnace, and the thickness of a coat was measured. From measurement using the analytical electron microscope which attaches characteristic-X-ray elemental-analysis equipment, the thickness of a coat was measured with about 18nm. It was shown from electron diffraction technique that a coat is film which makes an amorphous substance a subject. Moreover, into the coat, existence of the chlorine (Cl) of the minute amount presumed to be several 10 ppm was accepted.

[0024] After once taking out to the exterior and measuring thickness from halogen vapor growth equipment, Si single crystal substrate which put the coat of boron was laid in the interior of the MOCVD growth furnace provided to ordinary pressure (abbreviation atmospheric pressure) mold MOCVD vapor growth equipment. Then, the temperature of Si single crystal substrate was heated from the room temperature to 450 degrees C, circulating the hydrogen gas for conveyance of 8l./m (l) in a MOCVD growth furnace. When the temperature of Si single crystal substrate reached 450 degrees C, mixing of a phosphine (PH₃) was started to hydrogen carrier gas. The flow rate of PH₃ (100% of concentration) was adjusted to 400ml/m. The mixed ambient atmosphere of PH₃ and H₂ which makes PH₃ volume percentage and contains about 4.8% (it is made a partial pressure and is about 48.5hPa) from this was created. Lynn was made to permeate a coat the appropriate back, carrying out the temperature up of the temperature of Si single crystal substrate at the rate of 40 degrees C/m from 450 degrees C to 1050 degrees C. Warming of a substrate was stopped and lowered immediately after the temperature of Si single crystal substrate amounted to 1050 degrees C. PH₃ continued circulation in the MOCVD growth furnace by the above-mentioned flow rate until the temperature of a silicon single crystal substrate descended at 450 degrees C. When the temperature of a substrate became 450 degrees C, supply into the MOCVD growth furnace of PH₃ was suspended, and it stood by until it descended to the temperature near the room temperature within the ambient atmosphere which consists of only hydrogen carrier gas. After cooling, when the boron coat which performed the Lynn-ized processing from the MOCVD growth furnace was analyzed by electron diffraction technique, the result by which the boron coat is converted into Lynn-ized boron was shown. Thickness was about 16nm – about 18nm of a boron coat and an abbreviation EQC, and it was flat and it became what can fully be used as a continuous buffer coat without a crack.

[0025] Next, after Lynn-izing a boron coat within an ambient atmosphere including Lynn, the case where perform heat treatment and the Lynn-ized boron buffer coat is formed is made into an example, and the 3rd process of this invention is explained concretely.

[0026] With the aforementioned means, after performing the Lynn-ized processing to a boron coat within the mixed ambient atmosphere of PH₃ and H₂, it heat-treated by holding a substrate for 10 minutes in 1050 degrees C within the same ambient atmosphere. Then, the substrate was cooled to the temperature near the room temperature. When elemental analysis of the front face of the substrate which has the boron coat which

Lynn-ization-processed characteristic-X-ray elemental-analysis equipment using the involved analytical electron microscope was carried out, in the front face of the substrate which heat-treated, it was checked that Lynn (P) is distributed more over homogeneity as compared with the case where it does not heat-treat. moreover, about from secondary ion mass-spectrometry (SIMS) measurement 15- the depth direction of about 17nm boron coat — Lynn — abbreviation — having permeated uniformly was checked. That is, heat treatment concerning this invention was superficially effective in making Lynn permeate abbreviation homogeneity also in the depth direction to a boron coat.

[0027] Furthermore, on the Lynn-ized boron buffer coat formed via the 1st, 2nd, and 3rd process, the both sides of the source of boron and the source of Lynn are circulated, the case where vapor growth of the Lynn-ized boron system crystal layer is carried out is made into an example, and the 4th process of this invention is explained concretely.

[0028] Vapor growth of the Lynn-ized boron crystal layer was carried out on the Lynn-ized boron buffer coat in the MOCVD growth furnace, not performing cooling actuation of a substrate but maintaining the temperature of Si single crystal substrate at 1050 degrees C, after performing heat treatment at the 3rd above-mentioned process. The Lynn-ized boron crystal layer combined the hydrogen gas for foaming and PH₃ which accompanied the steam of boron triethyl (C₂H₅) (3B) to hydrogen carrier gas with a flow rate of 8l./m, was circulated in the MOCVD growth furnace, and was formed. 3(C₂H₅) B held at 25-degree C constant temperature was made to foam, and the flow rate of the hydrogen foaming gas which accompanies the steam was set to 45ml/m. The flow rate of PH₃ (100% of concentration) was set as 430ml/m. (C₂H₅) The hydrogen carrier gas containing the hydrogen gas and PH₃ which accompany the steam of 3B was continued for 8 minutes, it circulated, and the Lynn-ized boron crystal layer of p form was obtained by undoping on the Lynn-ized boron buffer coat. The thickness of the Lynn-ized boron crystal layer was about 420nm, and carrier concentration was abbreviation 2x10¹⁹cm⁻³. It depended on making the Lynn-ized boron buffer coat of this invention into a substrate, and membrane formation of the Lynn-ized boron crystal layer [****] by which a crack is not checked by looking, either was attained.

[0029] (The 2nd example) In the **** 2 example, with the same MOCVD vapor growth equipment as having made the boron coat form on a crystal substrate in the 1st process, the case where the 2nd, 3rd, and 4th processes are performed is made into an example, and the contents of this invention are explained concretely.

[0030] First, the coat which consists of boron was formed using ordinary pressure (abbreviation atmospheric pressure) mold MOCVD vapor growth equipment on the front face of an n form {111}-Si single crystal substrate. The temperature of Si single crystal substrate was maintained at 450 degrees C. The boron coat formed 3(C₂H₅) B as a source of boron. (C₂H₅) After making 3B foam with hydrogen gas, it was supplied. (C₂H₅) The temperature of 3B was maintained at 25 degrees C, and the flow rate of the hydrogen gas for foaming which accompanies the steam was adjusted to 10ml/m (ml). Moreover, the hydrogen gas for conveyance of 12l./m (l) was mixed, and the hydrogen gas for foaming which accompanies the steam of 3 (C₂H₅) B was supplied for 1.5 minutes in the MOCVD growth furnace provided to above MOCVD vapor growth equipment. (C₂H₅) Supply to the hydrogen carrier gas of the hydrogen gas for foaming which accompanies the steam of 3B was suspended, and the 1st process which forms a boron coat was ended. After ending the 1st process, for 30 seconds, we continued circulating only the hydrogen gas for conveyance, and decided to carry out the sweep of the above-mentioned source of boron which remains in a MOCVD growth furnace out of a furnace.

[0031] Then, mixing of PH₃ was started, circulating the hydrogen gas for conveyance of 12l./m (l) in the same MOCVD growth furnace as having made the boron coat put. The flow rate of PH₃ (100% of concentration) was adjusted to 430ml/m. The mixed ambient atmosphere of PH₃ and H₂ which makes PH₃ volume percentage and contains about 3.5% (it is made a partial pressure and they are about 35.0 hPaTorr(s)) from this was created.

Next, heating the temperature of Si single crystal substrate from 450 degrees C to 850 degrees C, Lynn was made to permeate a boron coat and the 2nd process which forms the Lynn-ized boron buffer coat was ended.

[0032] Then, it had the 3rd process which holds a substrate for 10 minutes at 850 degrees C within the mixed ambient atmosphere of above PH₃ and H₂, and heat treatment in which Lynn is made to permeate homogeneity was performed to the Lynn-ized boron buffer coat which depends on the 2nd process. The thickness of the buffer coat at the time of termination of the 3rd process was about 20nm of a boron coat and an abbreviation EQC, and was a continuation layer in flatness without a crack. moreover, the front face of the buffer coat from the Auger (Auger) spectral analysis — concentration — like — abbreviation — uniform — and the depth direction of about 20nm thickness — Lynn — abbreviation — having permeated uniformly was checked.

[0033] Next, the hydrogen gas for foaming which accompanies the steam of 3(C₂H₅) B was supplied in the same MOCVD growth furnace as having carried out the above-mentioned 1st thru/or the 3rd above-mentioned process, holding the temperature of a silicon single crystal substrate at 850 degrees C within the mixed ambient atmosphere of PH₃ (volume-percentage **3.5%) and H₂. The flow rate of the hydrogen gas for foaming which the hydrogen carrier gas of the above-mentioned flow rate was made to mix was set to 25ml/m. (C₂H₅) The hydrogen gas for conveyance containing the hydrogen gas for foaming which accompanies the steam of 3B, and PH₃ was supplied in the MOCVD growth furnace for 12 minutes, and the Lynn-ized boron crystal layer of n form was formed on the Lynn-ized boron buffer coat by undoping which sets thickness to

about 32nm. The carrier concentration of the Lynn-ized boron crystal layer was abbreviation $6 \times 10^{18} \text{cm}^{-3}$. Since the Lynn-ized boron buffer coat formed via the 1st thru/or the 3rd process was used as the substrate layer and ****, the 1st, or the 4th process was carried out using the same vapor growth furnace (MOCVD growth furnace), it became effective in bringing about the flat Lynn-ized boron crystal layer without a crack simple. Moreover, since we decided to perform a process in the same MOCVD growth furnace consistently and exposure to the open air of a boron coat was avoided, unlike the case of the 1st example, the sludge which becomes the front face of the Lynn-ized boron buffer coat from boron or the oxide of Lynn was not accepted.

[0034] (The 3rd example) After stopping circulation of the source of boron to a crystal substrate front face and ending the 1st process, the case where supply the source of Lynn immediately and the 2nd process is carried out is made into an example, and the contents of this invention are explained concretely.

[0035] After suspending supply into the MOCVD growth furnace of the source of boron and ending formation of the Lynn-ized boron buffer coat, there is no intermission, hydrogen carrier gas was made to mix PH₃, and it was made to circulate in the 2nd example. That is, PH₃ gas was circulated without preparing spacing for 30 seconds after termination of the 1st process established in the 2nd example in the **** 3 example, and it shifted to the 2nd process. Then, the 3rd thru/or the 4th process were carried out on the same conditions as the 2nd example, and the Lynn-ized boron crystal layer of n form was formed by undoping on the Lynn-ized boron buffer coat. In the front face of the Lynn-ized boron crystal layer, the spherical projection was not accepted but was flat. When depending on the analysis of the crystal structure using a general X-ray diffraction method, as shown in the X diffraction pattern of drawing 1, the Lynn-ized boron crystal layer was a continuation layer which consists of the {111} crystal faces which carried out orientation to <111> crystal orientation uniformly. Moreover, the thickness was the case of the 2nd example, and abbreviation identitas.

[0036] On the other hand, the thickness of the Lynn-ized boron buffer coat is about 25nm, and was thick about about 5nm as compared with the case of the 2nd example. Since this deleted the period exposed in the ambient atmosphere which consists only of hydrogen carrier gas, it was considered generating of the volatile component based on association with hydrogen and the boron which constitutes a boron coat should have been avoided, and fold. For example, formation of the volatile component based on association with a boron-bearing organic macromolecule object (refer to the Kajiwara *****, an "outline inorganic polymer" (April 10, Showa 53, the 1st ** of the 1st Edition of the Chijin Shokan Issue), and 53 pages) and hydrogen was avoided, and it was presumed to be the cause which keeps thickness thick that deviation from the coat of the boron based on volatilization was avoided.

[0037] (The 4th example) The case where the Lynn-ized boron system LED is constituted from the epitaxial laminating structure equipped with the Lynn-ized boron buffer coat and the Lynn-ized boron crystal layer concerning this invention is made into an example, and the contents of this invention are explained concretely.

[0038] The mimetic diagram of LED1B which starts **** 4 example at drawing 2 is shown. The structure of the cross section of LED1B in alignment with broken-line X-X' of drawing 2 is typically shown in drawing 3.

[0039] Epitaxial laminating structure 1A consisted of the Lynn-ized boron buffer coat 102 and the n form {111}-Lynn-ized boron crystal layer 103 which were formed like the 2nd above-mentioned example on the n form {111}-silicon single crystal substrate 101, and the luminous layer 104, the antilashing layer 105 and p form Lynn-ized boron crystal layer 106 which were prepared on this n form Lynn-ized boron crystal layer 103. The luminous layer 104 consisted of gallium nitride indium mixed-crystal (GaIn_{1-X}N) layers of n form. The GaIn_{1-X}N layer was formed at 850 degrees C using the trimethylgallium (CH₃)₃Ga / trimethylindium (CH₃)₃In / ammonia (NH₃) / H₂ system of reaction. Moreover, GaIn_{1-X}N was formed using the MOCVD vapor growth equipment in which n form Lynn-ized boron crystal layer 103 was formed. The indium presentation ratio of GaIn_{1-X}N of a hexagonal wurtzite crystal mold (=1-X) could be 10% so that it might become the lattice constant of the a-axis corresponding to spacing (*3.21Å) of the {110}-BP crystal face which intersects at a vertical the {111}-BP crystal face which makes the front face of the n form Lynn-ized boron (BP) crystal layer 103.

[0040] (CH₃) NH₃ was switched to PH₃, holding a substrate 101 at 850 degrees C, after suspending supply into the MOCVD growth furnace of 3Ga and (CH₃)₃In and ending formation of a luminous layer 104. The hydrogen gas for conveyance was made to mix the hydrogen gas for foaming which accompanies the steam of 3(C₂H₅) B in parallel, and it supplied in the MOCVD growth furnace in which the luminous layer 104 was formed. The flow rate of the hydrogen gas for foaming to 3(C₂H₅) B held to 25-degree C constant temperature was set to 10ml/m, and the flow rate of the hydrogen gas for conveyance was made into 12l/m (l). (C₂H₅) The hydrogen gas for foaming which accompanies the steam of 3B was circulated for 1 minute, it was made to join to a luminous layer 104, and n form Lynn-ized boron layer of undoping which sets thickness to about 15nm was prepared. This n form Lynn-ized boron layer is Ga_{0.90}In₀ which constitutes a luminous layer 104. It prepared as an antilashing layer 105 for preventing the vaporization of the indium (In) from 10Ns.

[0041] The addition to the hydrogen carrier gas of the hydrogen gas for foaming which accompanies the steam of 3(C₂H₅) B was once stopped the appropriate back, and the temperature up of the substrate 101 was carried out from 850 degrees C to 1050 degrees C in the mixed ambient atmosphere of PH₃ and H₂. After the temperature of a substrate 101 reached 1050 degrees C, the addition to the hydrogen carrier gas of the hydrogen gas for foaming which accompanies the steam of 3(C₂H₅) B was resumed, and the Lynn-ized boron

crystal layer 106 of p form was formed by undoping. The thickness of p form Lynn-ized boron crystal layer 106 could be about 210nm. moreover, usual electrolysis C-V — the carrier concentration of this layer 106 which depended on law and was measured — about 2 — it was $\times 10^{19} \text{cm}^{-3}$. (C2H5) After stopping the addition to the hydrogen carrier gas of the hydrogen gas for foaming which accompanies the steam of 3B and ending formation of p form Lynn-ized boron crystal layer 106, the temperature of laminating structure 1A was lowered at about 600 degrees C in the mixed ambient atmosphere of PH₃ and H₂. Then, supply of PH₃ into a MOCVD growth furnace was suspended, and laminating structure 1A was cooled to near the room temperature in H₂ air current.

[0042] The surface electrode 107 which consists of Au-Zn / nickel (nickel) / three-layer multistory structure of Au which has arranged the ohmic electrode which becomes a side in contact with this layer 106 from gold and a zinc (Au-Zn) alloy was formed in the center section of the p form Lynn-ized boron crystal layer 106 which makes the surface of laminating structure 1A. The surface electrode 107 which serves as the plinth (pad) electrode for connection was used as the circular electrode which sets a diameter to about 120 micrometers. Moreover, all over the abbreviation for the rear face of the n form Si single crystal substrate 101, the ohmic electrode which consists of aluminum (aluminum) as a rear-face electrode 108 has been arranged. The thickness of aluminum vacuum evaporatio no film could be about 2 micrometers. LED1B of the pn junction mold DH structure which pinched n form luminous layer 104 in p form and n form Lynn-ized boron crystal layers 106 and 103 consisted of this. Since the Lynn-ized boron layers 106 and 103 of the both sides of p form and n form had about 3eV as a band gap in a room temperature, each has used them effectively as a clad (clad) layer to a luminous layer 104.

[0043] When conduction of the operating current of 20mA (mA) was carried out between the surface electrode 107 and the rear-face electrode 108 in the forward direction, the violet band light which sets wavelength to about 440nm from LED1B was emitted. The brightness in the chip (chip) condition measured using a common integrating sphere became a 9mm candela (mcd), and LED1B of high luminescence reinforcement was offered. since [moreover,] pn junction was constituted from continuation film which excels [all / of n form luminous layer 104 and p form Lynn-ized boron layer 106] in surface surface smoothness — forward voltage (however, forward current = 20mA) — about 3 — the Lynn-ized boron system LED which has the good rectifying characteristic which sets to V and makes reverse voltage (however, reverse current = 10microA) more than 5V will be offered.

[0044]

[Effect of the Invention] It depends on the vapor growth which makes the compound which makes the compound containing boron the source of boron, and includes Lynn on the front face of a crystal substrate the source of Lynn. The Lynn-ized boron buffer coat, In the manufacture approach of the Lynn-ized boron system semi-conductor layer which forms the Lynn-ized boron system crystal layer which uses boron and Lynn as a configuration element on the Lynn-ized boron buffer coat The 1st process which carries out vapor growth of the coat which the source of boron is circulated on the front face of the crystal substrate held in the Lynn-ized boron buffer coat at the 1st temperature T1 (however, 250 degree-C \leq T1 \leq 750 degree C), and makes boron a subject on it, Since it went with the 2nd process which makes Lynn permeate the coat which makes boron a subject and formed within an ambient atmosphere including the source of Lynn at the 2nd temperature T2 (however, T1 \leq T2 \leq 1200 degree C), the Lynn-ized boron system crystal layer which is excellent in a continuity was able to be formed.

[0045] If it heat-treats to the Lynn-ized boron buffer coat which maintained the temperature of a crystal substrate beyond the 2nd temperature, and was formed via the 1st and 2nd processes as the 3rd process and the Lynn-ized boron buffer coat is especially formed in it within the ambient atmosphere which includes the source of Lynn after the 2nd process also superficially, the coat which becomes considering boron as a subject is uniformly permeated also in the depth direction in Lynn — it can make — the Lynn-ized boron system semiconducting crystal layer [**** / that a front face is flat and] — effectiveness can be raised for forming.

[0046] Moreover, on the Lynn-ized boron buffer coat formed via the 1st, 2nd, and 3rd process, the both sides of the source of boron and the source of Lynn are circulated, and by the approach including the 4th process to which vapor growth of the Lynn-ized boron system crystal layer is carried out, if the Lynn-ized boron system crystal layer is formed, the continuous Lynn-ized boron system crystal layer can be formed.

[0047] Moreover, since it carries out with the same vapor growth equipment with having carried out vapor growth of the coat which makes boron a subject for the 2nd, 3rd, and 4th processes at the 1st process, effectiveness is to form the Lynn-ized boron system crystal layer simple on a buffer coat.

[0048] Moreover, if the 2nd process is started and the Lynn-ized boron buffer coat is formed at the same time it stops circulation of the source of boron to a crystal substrate front face and terminates the 1st process, the Lynn-ized boron buffer coat which is excellent in a surface state can be formed, and if spread, effectiveness can be raised for forming the Lynn-ized boron system crystal layer which is excellent in a continuity.

[0049] Moreover, if the Lynn-ized boron system semiconductor device is constituted using the Lynn-ized boron buffer coat and the Lynn-ized boron system crystal layer concerning this invention, LED of high brightness which is excellent in a pn junction property, for example can be offered.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the X diffraction pattern of the Lynn-ized boron crystal layer concerning the 3rd example of this invention.

[Drawing 2] It is the mimetic diagram of LED concerning the 4th example of this invention.

[Drawing 3] It is a cross section in alignment with broken-line X-X' of LED shown in drawing 2 .

[Description of Notations]

1A Epitaxial laminating structure

1B LED

101 Silicon Single Crystal Substrate

102 Lynn-ized Boron Buffer Coat

103 N Form Lynn-ized Boron Crystal Layer

104 Luminous Layer

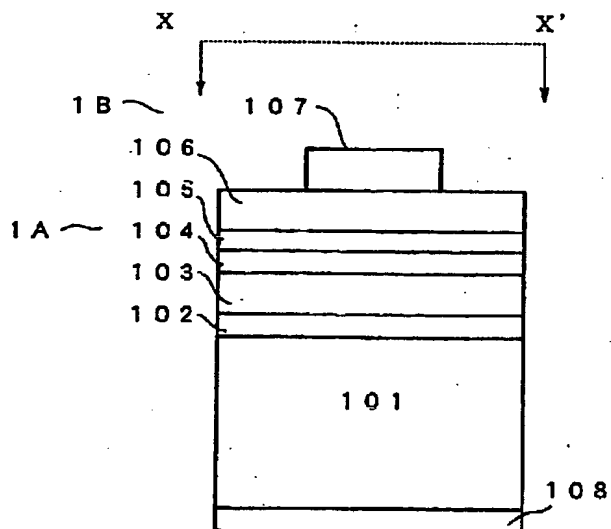
105 Antiflashing Layer

106 P Form Lynn-ized Boron Crystal Layer

107 Surface Electrode

108 Rear-Face Electrode

[Translation done.]



【特許請求の範囲】

【請求項1】 硼素（B）を含む化合物を硼素源とし、リン（P）を含む化合物をリン源とする気相成長法により、結晶基板の表面上に、リン化硼素からなる緩衝層（リン化硼素緩衝層）と、硼素及びリンを構成元素とするリン化硼素系結晶層とを順次形成するリン化硼素系半導体層の製造方法において、第1の温度 T_1 （但し、 $250^{\circ}\text{C} \leq T_1 \leq 750^{\circ}\text{C}$ ）に保持された結晶基板の表面に硼素源を流通させて、硼素を主体とする被膜を結晶基板の表面に気相成長させる第1の工程と、その後、結晶基板の温度を第2の温度 T_2 （但し、 $T_1 \leq T_2 \leq 1200^{\circ}\text{C}$ ）として、リン源を含む雰囲気内で、前記硼素を主体とする被膜にリンを浸透させる第2の工程とを経由して、結晶基板の表面上にリン化硼素緩衝層を形成することを特徴とするリン化硼素系半導体層の製造方法。

【請求項2】 第2の工程の後、リン源を含む雰囲気内で、結晶基板の温度を第2の温度 T_2 以上に維持し、リン化硼素緩衝層に熱処理を施す第3の工程を含むことを特徴とする請求項1に記載のリン化硼素系半導体層の製造方法。

【請求項3】 硼素源及びリン源の双方を同時に流通して、リン化硼素緩衝層上にリン化硼素系結晶層を気相成長させる第4の工程を含むことを特徴とする請求項2に記載のリン化硼素系半導体層の製造方法。

【請求項4】 第2、第3、第4の工程を、第1の工程において結晶基板の表面に硼素を主体とする被膜を気相成長させたのと同じ気相成長装置で行うことを特徴とする請求項3に記載のリン化硼素系半導体層の製造方法。

【請求項5】 結晶基板の表面への硼素源の流通を停止して第1の工程を終了させると同時に、雰囲気へリン源の供給を開始し第2の工程を開始することを特徴とする請求項4に記載のリン化硼素系半導体層の製造方法。

【請求項6】 硼素を主体とする被膜の膜厚が1nm以上100nm以下であることを特徴とする請求項1ないし5のいずれか1項に記載のリン化硼素系半導体層の製造方法。

【請求項7】 リン源の体積比率を3%以上とする雰囲気中で第2の工程を行うことを特徴とする請求項1ないし6のいずれか1項に記載のリン化硼素系半導体層の製造方法。

【請求項8】 第3の工程でリン化硼素緩衝層の熱処理を、5分間～40分間行うことを特徴とする請求項2ないし5のいずれか1項に記載のリン化硼素系半導体層の製造方法。

【請求項9】 結晶基板として、珪素（Si）単結晶を用いることを特徴とする請求項1ないし8のいずれか1項に記載のリン化硼素系半導体層の製造方法。

【請求項10】 請求項1ないし9のいずれか1項に記載のリン化硼素系半導体層の製造方法により製造したリン化硼素系半導体層。

【請求項11】 請求項10に記載のリン化硼素系半導体層を備えてなるリン化硼素系半導体素子。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、結晶基板の表面上に、リン化硼素からなる緩衝層（リン化硼素緩衝層）と、硼素及びリンを構成元素とするリン化硼素系結晶層とを順次形成するリン化硼素系半導体層の製造方法に係り、特に画一な配向方位を有するリン化硼素系結晶層を気相成長させるための技術に関する。

【0002】

【従来の技術】 従来より、硼素（B）とリン（P）とを構成元素とするリン化硼素系半導体層は、種々の半導体素子を構成するために利用されている。例えば、リン化硼素系半導体として代表的な単量体のリン化硼素（BP）からなる半導体層は、npn型ヘテロバイポーラトランジスタ（HBT）のn形ベース（base）層を構成するに利用されている（J. Electrochem. Soc., 125（4）（1978）、633～637頁参照）。また、青色のレーザダイオード（LD）にあつて、接触抵抗の低いオーミック（Ohmic）電極を形成するためのコンタクト（contact）層として利用されている（特開平10-242567号公報参照）。また、近紫外或いは青色等の短波長の発光をもたらす発光ダイオード（LED）を構成するための緩衝層として用いられている（米国特許6,069,021号参照）。

【0003】 上記の如くの半導体素子を構成するためのリン化硼素系半導体層は、従来より、気相成長手段により形成されている。従来からの気相成長手段には、三塩化硼素（ BCl_3 ）や三塩化リン（ PCl_3 ）を出発原料とするハロゲン（halogen）気相成長法（「日本結晶成長学会誌」、Vol. 24, No. 2（1997）、150頁参照）、ボラン（ BH_3 ）またはジボラン（ B_2H_6 ）とホスフィン（ PH_3 ）等を原料とするハイドライド（hydride）気相成長法（J. Crystal Growth, 24/25（1974）、193～196頁参照）、分子線エピタキシャル法（J. Solid State Chem., 133（1997）、269～272頁参照）、及び有機金属化学的気相堆積（MOCVD）法（Inst. Phys. Conf. Ser., No. 129（IOP Publishing Ltd.（UK、1993）、157～162頁参照））を例示できる。

【0004】 リン化硼素系半導体層を気相成長させるに際し、基板には半導体材料の単結晶を用いるのがもっぱらである。従来より、実用的な基板として、珪素（Si）単結晶（シリコン）（上記の①J. Electrochem. Soc., 125（1978）、及び②米国特許6,069,021号参照）、炭化珪素（SiC）

(特開平10-242569号公報参照)、リン化ガリウム(GaP)(特開平10-242568号公報参照)や窒化ガリウム(GaN)(特開平10-247745号公報参照)等の単結晶が用いられている。しかし、例えば、珪素単結晶の格子定数は 5.431\AA であり、閃亜鉛鉱型のBPのそれは 4.538\AA である(寺本 巖著、「半導体デバイス概論」(1995年3月30日、(株)培風館発行初版)、28頁参照)。従って、格子ミスマッチ度は約16.5%と大きく違っている(庄野 克房著、「半導体技術(上)」(1992年6月25日、(財)東京大学出版会発行9刷)、97~98頁参照)。

【0005】

【発明が解決しようとする課題】この様に格子ミスマッチ度を大とする結晶基板上では、リン化硼素系半導体層は、Volmer-Weber様の成長様式をもって島状の成長を起こす((社)応用物理学会薄膜・表面物理分科会編、「薄膜作製ハンドブック」(1991年3月25日、共立出版(株)発行初版第1刷)、59頁参照)。島状成長では、各成長島は、一定の結晶方位に沿って画一的に配向するとは限らない。このため、成長島を成長核として発達するリン化硼素系半導体層も、乱雑な配向性の結晶体から構成される不均質なものとなる欠点がある。或いは、Stranski-Krastanov様式状(上記の「薄膜作製ハンドブック」、59頁参照)の島状成長が誘因されるため、表面の平坦性に優れる連続性のあるリン化硼素系半導体層を安定して得るに支障を来している。

【0006】画一的な配向性の結晶体をもってなるリン化硼素系半導体層を提供するに有効な気相成長手段があれば、それを利用して、例えば、正常なpn接合特性を顕現でき、順方向電圧(所謂、 V_f)の低いLED、また、閾値電圧(所謂、 V_{th})の低いLDを簡便に提供できる。本発明では、特に、格子ミスマッチ度を大とする結晶基板上に、画一的な結晶面方位を有する連続性のあるリン化硼素系結晶層を簡便に且つ安定してもたすためのリン化硼素緩衝層の形成方法を提供する。また、その緩衝層並びにリン化硼素系結晶層を利用して構成したリン化硼素系半導体素子を提供する。

【0007】

【課題を解決するための手段】即ち、本発明は、

(1) 硼素(B)を含む化合物を硼素源とし、リン(P)を含む化合物をリン源とする気相成長法により、結晶基板の表面上に、リン化硼素からなる緩衝層(リン化硼素緩衝層)と、硼素及びリンを構成元素とするリン化硼素系結晶層とを順次形成するリン化硼素系半導体層の製造方法において、第1の温度 T_1 (但し、 $250^\circ\text{C} \leq T_1 \leq 750^\circ\text{C}$)に保持された結晶基板の表面に硼素源を流通させて、硼素を主体とする被膜を結晶基板の表面に気相成長させる第1の工程と、その後、結晶基板の

温度を第2の温度 T_2 (但し、 $T_1 \leq T_2 \leq 1200^\circ\text{C}$)として、リン源を含む雰囲気内で、前記硼素を主体とする被膜にリンを浸透させる第2の工程とを経由して、結晶基板の表面上にリン化硼素緩衝層を形成することを特徴とするリン化硼素系半導体層の製造方法。

(2) 第2の工程の後、リン源を含む雰囲気内で、結晶基板の温度を第2の温度 T_2 以上に維持し、リン化硼素緩衝層に熱処理を施す第3の工程を含むことを特徴とする上記(1)に記載のリン化硼素系半導体層の製造方法。

(3) 硼素源及びリン源の双方を同時に流通して、リン化硼素緩衝層上にリン化硼素系結晶層を気相成長させる第4の工程を含むことを特徴とする上記(2)に記載のリン化硼素系半導体層の製造方法。

(4) 第2、第3、第4の工程を、第1の工程において結晶基板の表面に硼素を主体とする被膜を気相成長させたのと同じ気相成長装置で行うことを特徴とする上記(3)に記載のリン化硼素系半導体層の製造方法。

(5) 結晶基板の表面への硼素源の流通を停止して第1の工程を終了させると同時に、雰囲気へリン源の供給を開始し第2の工程を開始することを特徴とする上記(4)に記載のリン化硼素系半導体層の製造方法。

(6) 硼素を主体とする被膜の膜厚が 1 nm 以上 100 nm 以下であることを特徴とする上記(1)ないし

(5)のいずれか1項に記載のリン化硼素系半導体層の製造方法。

(7) リン源の体積比率を3%以上とする雰囲気中で第2の工程を行うことを特徴とする上記(1)ないし

(6)のいずれか1項に記載のリン化硼素系半導体層の製造方法。

(8) 第3の工程でリン化硼素緩衝層の熱処理を、5分間~40分間行うことを特徴とする上記(2)ないし

(5)のいずれか1項に記載のリン化硼素系半導体層の製造方法。

(9) 結晶基板として、珪素(Si)単結晶を用いることを特徴とする上記(1)ないし(8)のいずれか1項に記載のリン化硼素系半導体層の製造方法。

である。

【0008】また、本発明は

(10) 上記(1)ないし(9)のいずれか1項に記載のリン化硼素系半導体層の製造方法により製造したリン化硼素系半導体層。

(11) 上記(10)に記載のリン化硼素系半導体層を備えてなるリン化硼素系半導体素子。

である。

【0009】

【発明の実施の形態】本発明のリン化硼素系半導体層の製造方法において、第1の工程は、硼素を含む化合物からなる硼素源を熱分解させて、硼素を主体とする被膜を結晶基板の表面に形成するための工程である。硼素源と

しては、三塩化硼素 (BCl_3) や三塩化臭素 (Br_3) 等のハロゲン化硼素化合物、ボラン (BH_3) またはジボラン (B_2H_6) 等の硼素水素化合物、或いはトリエチル硼素 ($(\text{C}_2\text{H}_5)_3\text{B}$) 等の有機硼素化合物を例示できる。これらの硼素源を加熱された結晶基板の表面に向けて供給し、硼素源の熱分解により放出された硼素を結晶基板に被着させて硼素を主体とした被膜を形成する。被膜には、硼素源の熱分解に因り発生した硼素以外の元素或いは分解生成物が含まれる場合がある。例えば、 $(\text{C}_2\text{H}_5)_3\text{B}$ を硼素源として形成した被膜には、硼素以外に炭素 (C) 或いは水素 (H) が含有される場合がある。硼素を主体とする被膜とは、硼素の重量含有量を 80% 以上とする被膜である。硼素を主体とする被膜の形成には、結晶基板の温度を 250°C 以上に保持するのが好適である。 250°C 未満の温度では硼素源の熱分解が充分に進行せず、硼素を主体とする被膜を安定して形成するには不都合である。また、 750°C を超える高温では、被膜を構成する硼素の凝縮が顕著に起こり、硼素を主体とする半球状の被膜が島状に結晶基板の表面に散在する状態を招く。このため、結晶基板の表面を均一に硼素を主体とする被膜で被覆するに至らず、後述する第 4 の工程で連続性のあるリン化硼素系結晶層を得るに難を来す。即ち、硼素を主体とする被膜を形成する第 1 の工程にあって、好適な温度 T_1 ($^\circ\text{C}$) は、 $250^\circ\text{C} \leq T_1 \leq 750^\circ\text{C}$ となる。

【0010】第 1 の工程において、硼素を主体とする被膜は複数種の硼素源を利用して形成できるが、硼素源を単一とすれば簡便に被膜を形成できて利便である。室温で液体である $(\text{C}_2\text{H}_5)_3\text{B}$ 等の硼素源は、水素等の発泡 (バブリング) 用気体に随伴させて被膜を形成するための気相成長装置内に供給できる。例えば、恒温に維持した $(\text{C}_2\text{H}_5)_3\text{B}$ を一定の時間、気相成長装置内に供給して被膜を形成する場合、硼素源を発泡するための気体の流量を増加させれば、被膜の膜厚は増加させられる。 $(\text{C}_2\text{H}_5)_3\text{B}$ 等の硼素源の蒸気を随伴する気体を、更に、搬送 (carrier) ガスと混合させて流通させれば、気相成長装置の内部により間断なく安定して硼素源を供給できる。搬送気体には、水素 (H_2)、窒素 (N_2) 並びにアルゴン (Ar) 等の単体ガスを利用できる。被膜の膜厚は 1nm 以上で 100nm 以下とするのが好ましい。 1nm 未満の極く薄膜では、硼素を主体とする被膜が結晶基板の表面を充分に均一に被覆するに至らず、第 4 の工程で結晶基板の表面を均一に被覆するリン化硼素系結晶層を得るに支障となる。また被膜の膜厚が 100nm を超える厚膜では、表面の平坦性に劣るため、第 4 の工程において、表面を平坦とし膜厚を均一とするリン化硼素系結晶層を得るに難を来す。また、膜厚を更に約 200nm を超える厚膜とすると、結晶基板から硼素を主体とする被膜が剥離する不都合を生ずる場合がある。硼素を主体とする被膜のさらに好適な

膜厚は、概して約 5nm ～ 約 50nm である。

【0011】第 2 の工程は、第 1 の工程で結晶基板の表面上に形成した硼素を主体とする被膜をリン源を含む雰囲気内で加熱して、被膜の内部にリンを浸透させて、硼素を主体とする被膜をリン化硼素からなる緩衝層に転化させるための工程である。リン源としては、三塩化リン (PCl_3) や三臭化リン (PBr_3) 等のハロゲン化リン化合物、ホスフィン (PH_3) 等のリン水素化合物、或いは有機リン化合物を例示できる。酸素 (O) を含むリン化合物は、被膜を主体的に構成する硼素、または被膜に浸透したリンに酸化作用を及ぼし、酸化物からなる析出物をもたらすため好ましいリン源とは成りかねる。リン源のみを流通させて雰囲気構成することもできるが、例えば、リン源を上記の搬送ガスと共に流通すると、リン源の濃度が調節された雰囲気を出出できる。例えば、第 1 の工程において被膜を形成した気相成長装置の内部に、 PH_3 と搬送ガスの水素の混合ガスを流通してリン源を含む雰囲気構成する。この場合、第 2 の工程を行う温度を考慮すると、雰囲気混合ガス中のリン源の体積比を 3% 以上とすると、硼素を主体とする被膜にリンを効率的に浸透させられる。被膜中に存在するリンの量は、例えば、2 次イオン質量分析 (SIMS) 法やオージェ電子分光法 (AES)、電子線プローブ (probe) X 線分析法等の元素分析法で定量できる。

【0012】第 2 の工程における結晶基板の温度 (第 2 の温度 T_2) は、第 1 の工程に於ける結晶基板の温度 (第 1 の温度 T_1) より高温で、且つ、 1200°C 以下の温度とする。 1200°C を超える高温では、例えば、菱面体結晶構造の B_{13}P_2 等のリン化硼素多量体の発生を招き (J. Am. Ceramic Soc., 47 (1) (1964)、44～46 頁参照)、上層として結晶性の揃ったリン化硼素系結晶層を得るに不都合となる。一方、 T_1 ($250^\circ\text{C} \leq T_1 \leq 750^\circ\text{C}$) 以下の温度では、リン源の熱分解が充分に進行しないため、硼素を主体とする被膜に浸透させるリンを効率的に放出できなくなり不都合である。よって、第 2 の工程で好適となる第 2 の温度 T_2 ($^\circ\text{C}$) は、 $T_1 \leq T_2 \leq 1200^\circ\text{C}$ の範囲である。リン源として PCl_3 等のハロゲン化リン化合物を使用した場合、熱分解で発生するハロゲン化合物に因り、硼素を主体とする被膜が食刻 (エッチング) される場合がある。食刻は高温である程、顕著となるため、ハロゲン化リン化合物をリン源とする際には、第 2 の工程に於ける第 2 の温度は、上記の好適な範囲内で比較的低温に設定するのが望ましい。即ち、概ね 950°C 以下とするのが好ましい。リン源に因る食刻が発生しない場合、第 2 の工程を終了した後に得られるリン化硼素層の膜厚は、第 1 の工程で形成した硼素を主体とする被膜の膜厚と略同となる。

【0013】本発明の第 1 の実施形態の好例としては、

第1の工程として、トリエチル硼素 ($(C_2H_5)_3B$) を硼素源に用いて、第1の温度 T_1 を $450^\circ C$ として、MOCVD成長装置内で、 $\{111\}$ 結晶面を有する珪素単結晶基板 ($\{111\}$ -珪素単結晶基板) の表面上に、膜厚を約 20 nm とする硼素からなる被膜を気相成長させ、その後第2の工程として、体積百分率にして6%のホスフィン (PH_3) を含む水素雰囲気中で、基板の温度を $450^\circ C$ から第2の温度 ($=T_2$) である $1050^\circ C$ に昇温しつつ、上記の硼素からなる被膜にリンを浸透させる工程を経由して、リン化硼素層を形成する手法を挙げられる。第1及び第2の工程を経て形成されたリン化硼素層は、結晶基板との格子ミスマッチを緩和して結晶性に優れる上層をもたらすに有効な緩衝層として作用できる。この緩衝層は、従来の硼素源とリン源とを結晶基板の表面に併せて供給して気相成長させた低温緩衝層 (上記の米国特許6,069,021号参照) よりも、更に表面の平坦性に優れたリン化硼素系結晶層をもたらせる緩衝層として作用する。また、画一的な結晶方

$$\log P = -(13.7 \times 10^3 / T) + 10.2 \quad \dots \dots \text{関係式(1)}$$

熱処理に依る組成の均一化或いは配向性の画一化の効果は、当量的に見合わない化学量論的に不均衡な組成のリン化硼素についても達成され得る。

【0015】本発明の第2の実施形態の好例として、第1及び第2の工程を経過して形成したリン化硼素からなる緩衝層に対して、第3の工程において、第2の工程の第2の温度と同じ $950^\circ C$ で、体積百分率にして10%の PH_3 を含む PH_3 と Ar の混合ガスからなる雰囲気中で、15分間に亘る熱処理を施す手法を挙げられる。熱処理に依る効果は、熱処理温度を第2の工程の第2の温度以上とすることに依り顕著に発現できる。但し、 $1200^\circ C$ を超える高温での熱処理は $B_{13}P_2$ 等の多量体の発生を来とし、結局のところ結晶型を相違する不均質なリン化硼素緩衝層をもたらすため好ましくはない。第3の工程の熱処理時間としては、およそ5分間~40分間とするのが好適である。第3の工程に係わる熱処理は、一定の温度に一定の時間に亘り保持する手段に限定されない。例えば、或る温度 T_2 より別の温度へ昇温または降温しつつ、熱処理を施す手法もある。本発明の第2の実施形態の別の例として、例えば、第2の温度を $900^\circ C$ として第2の工程を終了した後、体積百分率にして8%の PH_3 を含む PH_3 と N_2 の混合ガスからなる雰囲気中で、リン化硼素緩衝層の温度を $1100^\circ C$ まで毎分 $20^\circ C$ の速度で昇温して、10分間に亘り熱処理を施す手法を挙げられる。急激な速度での昇温または降温は、却って、緩衝層に熱的歪を導入することとなる。逆に、緩慢な速度での昇温または降温は緩衝層からのリンの揮発の機会を徒に増やし、リンの逸脱に因る緩衝層の表面の乱雑化を助長するに過ぎない。このような問題を排除するに好適となる昇温或いは降温速度は概して、毎分約 $10^\circ C$ から毎分約 $50^\circ C$ の範囲にある。

位の結晶面からなるリン化硼素系結晶層を上層としてもたらし作用を発揮する。

【0014】緩衝層として有効に作用するリン化硼素緩衝層を、上記の第1及び第2の工程を経由して形成した後、更に、リン源を含む雰囲気内で熱処理 (anneal) を施すことにより、該リン化硼素緩衝層をリン組成の均一な、しかも、配向性の揃った緩衝層となすことができる。低温ではリン源の熱分解が十分に進行せず、また、高温ではリン化硼素多量体の発生を誘引するため、熱処理温度は、第2の温度 T_2 (但し、 $T_1 \leq T_2 \leq 1200^\circ C$) 以上とするのが適する。雰囲気は、その熱処理を施す温度において、少なくとも、リン化硼素から解離するリン分子の圧力を超える分圧のリン源を含有している必要がある。リン化硼素の解離圧 (P ; 単位 hPa) は、温度を T (単位: K) として次記の関係式 (1) より求められるとされる (J. Am. Chem. Soc., 82 (1960), 1330~1332頁参照)。

$$\log P = -(13.7 \times 10^3 / T) + 10.2 \quad \dots \dots \text{関係式(1)}$$

【0016】上記の如く、第1及び第2の工程を経由して形成したリン化硼素層は、結晶基板との格子ミスマッチを緩和する緩衝層として有効に利用できる。従って、この緩衝層上には結晶欠陥の少ない結晶性を良好とするリン化硼素系結晶層を成長させられる。リン化硼素系結晶層とは、硼素とリンとを構成元素として含む、例えば $B_\alpha Al_\beta Ga_\gamma In_{1-\alpha-\beta-\gamma} P_{1-\delta} As_\delta$ ($0 < \alpha \leq 1, 0 \leq \beta < 1, 0 \leq \gamma < 1, 0 < \alpha + \beta + \gamma \leq 1, 0 \leq \delta < 1$)、また例えば、 $B_\alpha Al_\beta Ga_\gamma In_{1-\alpha-\beta-\gamma} P_{1-\delta} N_\delta$ ($0 < \alpha \leq 1, 0 \leq \beta < 1, 0 \leq \gamma < 1, 0 < \alpha + \beta + \gamma \leq 1, 0 \leq \delta < 1$) である。半導体素子を構成するための機能層として利用するためには、これらのリン化硼素系結晶層は化学量論的に均衡の取れているのが好適である。従って、第1の工程においてリン化硼素緩衝層を気相成長させる場合とは異なり、リン化硼素系結晶層は、硼素源及びリン源の双方を同時に流通してリン化硼素緩衝層上に形成する。本発明の第3の実施形態の一例として、リン化硼素 (BP) 緩衝層上に、第4の工程として、 $(C_2H_5)_3B$ とトリメチルガリウム ($(CH_3)_3Ga$) と PH_3 とを並行して流通しつつ、MOCVD法に依り間接遷移型の $B_xGa_{1-x}P$ ($0 \leq x \leq 1$) 層を気相成長させる例を挙げられる。

【0017】第1の工程で硼素を主体とする被膜の形成を硼素源の供給を停止して終了させた後、代替にリン源を供給して、同一の気相成長装置において、引き続き第2の工程を進行させることとすると、簡便にリン化硼素緩衝層を気相成長させられる。この手法に依れば、第1の工程を終了後、硼素を主体とする被膜を大気に曝すことなく第2の工程に移行できるので、例えば、硼素化合物の形成に因り、被膜表面の平滑性を損なわれるのを防止できる。また、第2の工程に引き続き第3及び第4の

工程を同一の気相成長装置で実施すれば、間断無く第2、第3及び第4の工程を簡易に遂行できる利点がある。また、第1から第4に至る工程に同一の硼素源とリン源を用れば尚更のこと、簡便にリン化硼素系半導体層を形成できる。本発明の第4の実施形態の好例として、ジボラン (B_2H_6) とホスフィン (PH_3) とを共通の原料として、第1、第2、第3および第4の工程を同一のハイドライド気相成長装置内で実施する場合を挙げられる。

【0018】第1の工程で硼素を主体とする被膜の形成に使用した硼素源の供給を停止して、直ちに、第2の工程のための第2の温度に昇温しつつ、併せて、リン源の供給を開始すると、結晶面方位を画一的とするリン化硼素系結晶層を与えるリン化硼素緩衝層を構成できる。特に、結晶基板表面の結晶面と同一の結晶面から画一的になる結晶層が得られる。例えば、{111}-珪素単結晶基板上に、{111}結晶面から画一的になるリン化硼素系結晶層をもたせるリン化硼素緩衝層を提供できる。第1の工程に使用した硼素源の供給を停止した後、リン源の供給を開始する迄に約1分間を超える長時間の間隔を設けると、結晶面方位を相違する結晶が混在するリン化硼素系結晶層を時として与えるリン化硼素緩衝層が帰結される場合がある。これは、硼素源の供給を停止して暫時、被膜を搬送ガスだけの雰囲気内で放置した際に形成される多角形状或いは球状の硼素体の発生に起因するものと思量される。この様な球状の硼素体の発生の状況は既に公開されている刊行物に見て取れる (J. Solid State Chem., 133 (1997), 314~321頁にあって、特に、316頁に掲載のFIG. 2)。本発明の第5の実施形態の一例として、第1の工程で使用した $(C_2H_5)_3B$ の硼素源の供給を停止すると同時に、 PH_3 を第1の工程で利用したMOCVD気相成長装置内に供給して、第2の工程を直ちに開始する手法を挙げられる。

【0019】本発明の第1及び第2の工程を経由して形成されたリン化硼素緩衝層上には、第4の工程に依り、結晶性に優れたリン化硼素系結晶層を設けることができる。この結晶性の良好なリン化硼素系結晶層を下地層とすれば、その上層も結晶性に優れたものとなる。これらの結晶性の良いリン化硼素系結晶層或いは上層を種々の機能層として活用すれば、特性に優れたリン化硼素系半導体素子を構成できる。本発明の第6の実施形態の一例として、珪素単結晶基板上に設けた次の(a)~(e)に記載の各機能層を備えたエピタキシャル積層構造体からpn接合型リン化硼素系半導体LEDを構成する場合を挙げられる。

(a) 第1の工程で形成した硼素被膜に、第2の工程でリンを浸透させた後、第3の工程で熱処理を施してリンを均一に分布させてなるリン化硼素緩衝層

(b) 第4の工程で硼素源とリン源とを同時に供給する

気相成長法に依り形成した、例えば、不純物を添加していない所謂、アンドープ (undoped) のリン化硼素結晶層からなるp形下部クラッド層

(c) 第1乃至第4の工程で使用したMOCVD成長装置を使用して、前項(b)に記載の下部クラッド層に接合させて気相成長させた窒化ガリウム・インジウム ($Ga_xIn_{1-x}N$: $0 \leq x \leq 1$) からなるn形発光層

(d) 同じく同一のMOCVD成長装置を使用して、前項(c)の発光層に接合させて設けたアンドープでn形のリン化硼素からなる発光層からのインジウム (In) の揮発を抑制するための蒸発防止層

(e) 同じく同一のMOCVD成長装置を使用して、前項(d)の蒸発防止層に接合させて設けたアンドープでn形のリン化硼素からなる上部クラッド層

さらに上記の(a)~(e)に記載の各機能層を備えたエピタキシャル積層構造体の導電性の珪素単結晶基板の裏面と、この積層構造体の最表層の上部クラッド層に接して互いに極性を異にするオーミック電極を各々、設けてLEDを構成することができる。

【0020】

【作用】本発明の第1の工程で形成された硼素を主体とする被膜は、後に、結晶基板の表面を一樣に均一に被覆する、表面の平坦性に優れたリン化硼素緩衝層をもたらし作用を発揮する。

【0021】本発明の第2の工程に於けるリン源を含む雰囲気は、硼素を主体とする被膜にリンを浸透させて、硼素を主体とする被膜をリン化硼素緩衝層に転化する作用を有する。

【0022】

【実施例】(第1実施例) 珪素単結晶基板上に形成した硼素の被膜からリン化硼素層を形成する例を用いて、まず本発明の第1の工程および第2の工程を具体的に説明する。

【0023】本第1実施例では、一般的なハロゲン気相成長装置 (例えば、(社)電子通信学会「半導体・トランジスタ研究会資料/資料番号SSD74-89 (1975-03) (1975年3月25日) 参照) を利用して、p形{111}-Si単結晶基板の表面上に、第1の工程として硼素からなる被膜を形成した。Si単結晶基板の温度は350℃に維持した。硼素の被膜は、三塩化硼素 (BCl_3) を硼素源として形成した。 BCl_3 は水素ガスで発泡させた後に気相成長装置に供給した。 BCl_3 の温度は0℃に維持し、その蒸気を随伴する発泡用水素ガスの流量は毎分15ミリリットル (ml) に調整した。また、 BCl_3 の蒸気を随伴する発泡用水素ガスは、毎分8リットル (l) の搬送用水素ガスに混合させて、8分間に亘り、上記のハロゲン気相成長装置に具備されている気相成長炉内に供給した。 BCl_3 の蒸気を随伴する発泡用水素ガスの水素搬送ガスへの供給を停止し、硼素の被膜を形成する第1の工程を終了して、基

板を室温近傍の温度に冷却した。その後、硼素の被膜を被着させたSi単結晶基板を気相成長炉から取出して、被膜の膜厚を測定した。特性X線元素分析装置を付帯する分析電子顕微鏡を利用した測定から、被膜の膜厚は約18nmと計測された。電子線回折技法から被膜は、非晶質を主体とする膜であるのが示された。また、被膜中には数10ppmと推定される微量の塩素(Cl)の存在が認められた。

【0024】ハロゲン気相成長装置より一旦、外部へ取り出して膜厚を測定した後、硼素の被膜を被着したSi単結晶基板を常圧(略大気圧)型MOCVD気相成長装置に具備されたMOCVD成長炉の内部に載置した。その後、MOCVD成長炉内に毎分8リットル(1)の搬送用水素ガスを流通しつつ、Si単結晶基板の温度を室温から450℃へと加熱した。Si単結晶基板の温度が450℃に到達した時点で、水素搬送ガスへホスフィン(PH₃)の混合を開始した。PH₃(濃度100%)の流量は毎分400mlに調整した。これより、PH₃を体積百分率にして約4.8%(分圧にして約48.5hPa)を含むPH₃とH₂の混合雰囲気を出した。その後、Si単結晶基板の温度を450℃から1050℃へ毎分40℃の速度で昇温しつつ、被膜にリンを浸透させた。Si単結晶基板の温度が1050℃に達した直後に、基板の加温を停止して降温した。PH₃は珪素単結晶基板の温度が450℃に降下する迄、上記の流量でMOCVD成長炉内に流通を継続した。基板の温度が450℃となった時点でPH₃のMOCVD成長炉内への供給を停止し、水素搬送ガスのみから構成される雰囲気内で室温近傍の温度に降下する迄、待機した。冷却後、MOCVD成長炉からリン化処理を施した硼素被膜を電子線回折技法により解析したところ、硼素被膜はリン化硼素に転化されている結果が示された。層厚は硼素被膜と略同等の約16nm〜約18nmであり、亀裂の無い平坦で連続性のある緩衝層として十分に利用できるものとなった。

【0025】次に硼素被膜をリンを含む雰囲気内でリン化した後、熱処理を施してリン化硼素緩衝層を形成する場合を例にして、本発明の第3の工程を具体的に説明する。

【0026】前記の手段により、硼素被膜にPH₃とH₂の混合雰囲気内でリン化処理を施した後、同じ雰囲気内で1050℃において10分間に亘り基板を保持し、熱処理を施した。その後、基板を室温近傍の温度に冷却した。特性X線元素分析装置を付帯する分析電子顕微鏡を利用して、リン化処理した硼素被膜を有する基板の表面の元素分析を実施したところ、熱処理を行った基板の表面には、熱処理をしなかった場合と比較してより均一にリン(P)が分布しているのが確認された。また、2次イオン質量分析法(SIMS)測定からは、約15〜約17nmの硼素被膜の深さ方向にリンが略一様に浸透し

ているのが確認された。即ち、本発明に係わる熱処理は、硼素被膜に平面的にも深さ方向にも略均一にリンを浸透させるに有効であった。

【0027】さらに、第1、第2、第3の工程を経由して形成したリン化硼素緩衝層上に、硼素源及びリン源の双方を流通して、リン化硼素系結晶層を気相成長させる場合を例にして本発明の第4の工程を具体的に説明する。

【0028】上記の第3の工程での熱処理を施した後、基板の冷却操作を施さず、Si単結晶基板の温度を1050℃に維持したままで、MOCVD成長炉内でリン化硼素結晶層をリン化硼素緩衝層上に気相成長させた。リン化硼素結晶層は、毎分8lの流量の水素搬送ガスに、トリエチル硼素((C₂H₅)₃B)の蒸気を随伴した発泡用水素ガスとPH₃とを併せて、MOCVD成長炉内に流通させて形成した。25℃の恒温に保持された(C₂H₅)₃Bを発泡させ、その蒸気を随伴する水素発泡ガスの流量は毎分45mlとした。PH₃(濃度100%)の流量は毎分430mlに設定した。(C₂H₅)₃Bの蒸気を随伴する水素ガス及びPH₃を含む水素搬送ガスを8分間に亘り継続して流通して、リン化硼素緩衝層上にアンドープでp形のリン化硼素結晶層を得た。リン化硼素結晶層の層厚は約420nmであり、キャリア濃度は約2×10¹⁹cm⁻³であった。本発明のリン化硼素緩衝層を下地とすることに依り、亀裂も視認されない連続なリン化硼素結晶層の成膜が可能となった。

【0029】(第2実施例)本第2実施例では、第1の工程において硼素被膜を結晶基板上に形成させたのと同じMOCVD気相成長装置で、第2、第3及び第4の工程を行う場合を例にして、本発明の内容を具体的に説明する。

【0030】先ず、常圧(略大気圧)型MOCVD気相成長装置を利用して、n形{111}-Si単結晶基板の表面上に、硼素からなる被膜を形成した。Si単結晶基板の温度は450℃に維持した。硼素被膜は、(C₂H₅)₃Bを硼素源として形成した。(C₂H₅)₃Bは水素ガスで発泡させた後に供給した。(C₂H₅)₃Bの温度は25℃に維持し、その蒸気を随伴する発泡用水素ガスの流量は毎分10ミリリットル(ml)に調整した。また、(C₂H₅)₃Bの蒸気を随伴する発泡用水素ガスは、毎分12リットル(1)の搬送用水素ガスに混合させて、1.5分間に亘り、上記のMOCVD気相成長装置に具備されているMOCVD成長炉内に供給した。

(C₂H₅)₃Bの蒸気を随伴する発泡用水素ガスの水素搬送ガスへの供給を停止し、硼素被膜を形成する第1の工程を終了した。第1の工程を終了した後、30秒間に亘り、搬送用水素ガスのみを流通し続け、MOCVD成長炉内に残存している上記の硼素源を炉外へ掃引することとした。

【0031】その後、硼素被膜を被着させたのと同じ一

MOCVD成長炉内に、毎分12リットル(1)の搬送用水素ガスを流通しつつ、 PH_3 の混合を開始した。 PH_3 (濃度100%)の流量は毎分430mlに調整した。これより、 PH_3 を体積百分率にして約3.5%(分圧にして約35.0hPa Torr)を含む PH_3 と H_2 の混合雰囲気を出した。次に、Si単結晶基板の温度を450℃から850℃に加熱しつつ、硼素被膜にリンを浸透させて、リン化硼素緩衝層を形成する第2の工程を終了した。

【0032】引き続き、上記の PH_3 と H_2 の混合雰囲気内で850℃に10分間に亘り基板を保持する第3の工程をもって、第2の工程に依るリン化硼素緩衝層にリンを均一に浸透させる熱処理を施した。第3の工程の終了時に於ける緩衝層の層厚は硼素被膜と略同等の約20nmであり、亀裂の無い平坦で連続層であった。また、オージェ(Auger)分光分析からは、緩衝層の表面に濃度的に略一様に、且つ、約20nmの層厚の深さ方向にリンが略一様に浸透しているのが確認された。

【0033】次に、 PH_3 (体積百分率≒3.5%)と H_2 の混合雰囲気内で珪素単結晶基板の温度を850℃に保持しつつ、上記の第1乃至第3の工程を実施したのと同じMOCVD成長炉内に、 $(\text{C}_2\text{H}_5)_3\text{B}$ の蒸気を随伴する発泡用水素ガスを供給した。上記の流量の水素搬送ガスに混合させた発泡用水素ガスの流量は毎分25mlとした。 $(\text{C}_2\text{H}_5)_3\text{B}$ の蒸気を随伴する発泡用水素ガスと PH_3 とを含む搬送用水素ガスを12分間に亘り、MOCVD成長炉内に供給して、層厚を約32nmとするアンドープでn形のリン化硼素結晶層をリン化硼素緩衝層上に形成した。リン化硼素結晶層のキャリア濃度は約 $6 \times 10^{18} \text{ cm}^{-3}$ であった。第1乃至第3の工程を経由して形成したリン化硼素緩衝層を下地層とし、尚且、第1乃至第4の工程を同一の気相成長炉(MOCVD成長炉)を利用して実施したため、亀裂のない平坦なリン化硼素結晶層を簡便にもたすに有効となった。また、工程を一貫して同一のMOCVD成長炉内で行うこととし、硼素被膜の外気への暴露を回避したため、第1の実施例の場合とは異なり、リン化硼素緩衝層の表面に、硼素或いはリンの酸化物からなる析出物は認められなかった。

【0034】(第3実施例) 結晶基板表面への硼素源の流通を停止して第1の工程を終了した後、直ちにリン源を供給して第2の工程を実施する場合を例にして、本発明の内容を具体的に説明する。

【0035】第2実施例において、硼素源のMOCVD成長炉内への供給を停止してリン化硼素緩衝層の形成を終了した後、間断無く、 PH_3 を水素搬送ガスに混合させて流通させた。即ち、第2実施例で設けた第1の工程の終了後の30秒間の間隔を、本第3実施例では設けずに PH_3 ガスを流通させ、第2の工程に移行した。その後、第2実施例と同一の条件で第3乃至第4の工程を実

施し、リン化硼素緩衝層上にアンドープでn形のリン化硼素結晶層を形成した。リン化硼素結晶層の表面には、球状の突起物は認められず、平坦であった。一般的なX線回折法を利用した結晶構造の解析に依れば、図1のX線回折パターンに示す如く、リン化硼素結晶層は<111>結晶方向に画一的に配向した{111}結晶面からなる連続層であった。また、その層厚は第2実施例の場合と略同一であった。

【0036】一方、リン化硼素緩衝層の層厚は約25nmとなっており、第2実施例の場合と比較して約5nm程、厚くなっていた。これは、水素搬送ガスのみからなる雰囲気内に暴露される期間を削除したため、水素と硼素被膜を構成する硼素との結合に因る揮発性の成分の発生が回避されたためと思量された。例えば、含硼素有機高分子体(梶原 鳴雪著、「概説無機高分子」(昭和53年4月10日、(株)地人書館発行第1版第1刷)、53頁参照)と水素との結合に因る揮発性成分の形成が回避され、揮発に因る硼素の被膜からの逸脱が避けられたのが層厚を厚く保つ一因と推定された。

【0037】(第4実施例) 本発明に係るリン化硼素緩衝層及びリン化硼素結晶層を備えたエピタキシャル積層構造体からリン化硼素系LEDを構成する場合を例にして、本発明の内容を具体的に説明する。

【0038】図2に本第4実施例に係るLED1Bの平面模式図を示す。図3には、図2の破線X-X'に沿ったLED1Bの断面の構造を模式的に示す。

【0039】エピタキシャル積層構造体1Aは、n形{111}-珪素単結晶基板101上に上記の第2実施例と同様に形成したリン化硼素緩衝層102及びn形{111}-リン化硼素結晶層103と、該n形リン化硼素結晶層103上に設けた発光層104、蒸発防止層105及びp形リン化硼素結晶層106とから構成した。発光層104は、n形の窒化ガリウム・インジウム混晶($\text{Ga}_x\text{In}_{1-x}\text{N}$)層から構成した。 $\text{Ga}_x\text{In}_{1-x}\text{N}$ 層は、トリメチルガリウム($(\text{CH}_3)_3\text{Ga}$)/トリメチルインジウム($(\text{CH}_3)_3\text{In}$)/アンモニア(NH_3)/ H_2 反応系を利用して850℃で形成した。また、 $\text{Ga}_x\text{In}_{1-x}\text{N}$ は、n形リン化硼素結晶層103を形成したMOCVD気相成長装置を使用して形成した。六方晶ウルツ鉱結晶型の $\text{Ga}_x\text{In}_{1-x}\text{N}$ のインジウム組成比($=1-x$)は、n形リン化硼素(BP)結晶層103の表面をなす{111}-BP結晶面に鉛直に交差する{110}-BP結晶面の間隔($\approx 3.21 \text{ \AA}$)に合致するa軸の格子定数となるように10%とした。

【0040】 $(\text{CH}_3)_3\text{Ga}$ 及び $(\text{CH}_3)_3\text{In}$ のMOCVD成長炉内への供給を停止して発光層104の形成を終了した後、基板101を850℃に保持しつつ、 NH_3 を PH_3 に切り換えた。並行して $(\text{C}_2\text{H}_5)_3\text{B}$ の蒸気を随伴する発泡用水素ガスを搬送用水素ガスに混合させて、発光層104を形成したMOCVD成長炉内に供

給した。25℃の恒温に保持した $(C_2H_5)_3B$ への発泡用水素ガスの流量は毎分10mlとし、搬送用水素ガスの流量は毎分12リットル(1)とした。 $(C_2H_5)_3B$ の蒸気を随伴する発泡用水素ガスを1分間に亘り流通して、膜厚を約15nmとするアンドープのn形リン化硼素層を発光層104に接合させて設けた。このn形リン化硼素層は発光層104を構成する $Ga_{0.90}In_{0.10}N$ からのインジウム(In)の揮散を防止するための蒸発防止層105として設けた。

【0041】然る後、一旦、 $(C_2H_5)_3B$ の蒸気を随伴する発泡用水素ガスの水素搬送ガスへの添加を中止して、 PH_3 と H_2 の混合雰囲気中で基板101を850℃から1050℃へ昇温した。基板101の温度が1050℃に到達した後、 $(C_2H_5)_3B$ の蒸気を随伴する発泡用水素ガスの水素搬送ガスへの添加を再開して、アンドープでp形のリン化硼素結晶層106を形成した。p形リン化硼素結晶層106の層厚は約210nmとした。また、通常の電解C-V法に依り測定された同層106のキャリア濃度は約 $2 \times 10^{19} cm^{-3}$ であった。

$(C_2H_5)_3B$ の蒸気を随伴する発泡用水素ガスの水素搬送ガスへの添加を停止して、p形リン化硼素結晶層106の形成を終了した後、 PH_3 と H_2 の混合雰囲気中で積層構造体1Aの温度を約600℃に降温した。その後、MOCVD成長炉内への PH_3 の供給を停止し、 H_2 気流中で積層構造体1Aを室温近傍迄、冷却した。

【0042】積層構造体1Aの表層をなすp形リン化硼素結晶層106の中央部には、同層106に接触する側に金・亜鉛(Au・Zn)合金からなるオーミック電極を配置したAu・Zn/ニッケル(Ni)/Auの3層重層構造からなる表面電極107を設けた。結線用の台座(pad)電極を兼ねる表面電極107は、直径を約120μmとする円形の電極とした。また、n形Si単結晶基板101の裏面の略全面には、裏面電極108としてアルミニウム(Al)からなるオーミック電極を配置した。Al蒸着膜の膜厚は約2μmとした。これより、n形発光層104をp形及びn形リン化硼素結晶層106、103で挟持したpn接合型DH構造のLED1Bを構成した。p形及びn形の双方のリン化硼素層106、103は何れも、室温での禁止帯幅として約3eVを有するため、発光層104に対するクラッド(clad)層として有効に利用できた。

【0043】表面電極107と裏面電極108との間に順方向に20ミリアンペア(mA)の動作電流を通流したところ、LED1Bから波長を約440nmとする青紫帯光が発せられた。一般的な積分球を利用して測定されるチップ(chip)状態での輝度は9ミリカンデラ(mcd)となり、高発光強度のLED1Bが提供された。また、n形発光層104とp形リン化硼素層106との何れも表面の平坦性に優れる連続膜からpn接合を構成したため、順方向電圧(但し、順方向電流=20m

A)を約3Vとし、逆方向電圧(但し、逆方向電流=10μA)を5V以上とする良好な整流特性を有するリン化硼素系LEDが提供されることとなった。

【0044】

【発明の効果】結晶基板の表面上に、硼素を含む化合物を硼素源とし、また、リンを含む化合物とをリン源とする気相成長法に依り、リン化硼素緩衝層と、リン化硼素緩衝層上に、硼素及びリンを構成元素とするリン化硼素系結晶層とを形成するリン化硼素系半導体層の製造方法において、リン化硼素緩衝層を、第1の温度 T_1 (但し、 $250^\circ C \leq T_1 \leq 750^\circ C$)に保持された結晶基板の表面に、硼素源を流通させて、硼素を主体とする被膜を気相成長する第1の工程と、第2の温度 T_2 (但し、 $T_1 \leq T_2 \leq 1200^\circ C$)で、リン源を含む雰囲気内で、硼素を主体とする被膜にリンを浸透させる第2の工程とを経由して形成することとしたので、連続性に優れるリン化硼素系結晶層を形成することが出来た。

【0045】特に第2の工程の後、リン源を含む雰囲気内で、結晶基板の温度を第2の温度以上に維持し、第1及び第2の工程を経由して形成したリン化硼素緩衝層に、第3の工程として熱処理を施してリン化硼素緩衝層を形成すると、硼素を主体としてなる被膜へリンを平面的にも深さ方向へも一様に浸透させることができ、表面が平坦で連続なリン化硼素系半導体結晶層の形成するに効果を上げられる。

【0046】また、第1、第2、第3の工程を経由して形成したリン化硼素緩衝層上に、硼素源及びリン源の双方を流通して、リン化硼素系結晶層を気相成長させる第4の工程を含む方法によって、リン化硼素系結晶層を形成すると、連続性のあるリン化硼素系結晶層を形成することができる。

【0047】また、第2、第3及び第4の工程を、第1の工程で硼素を主体とする被膜を気相成長させたと同一の気相成長装置で行うこととしたので、緩衝層上に簡便にリン化硼素系結晶層を形成するに効果がある。

【0048】また、結晶基板表面への硼素源の流通を停止して第1の工程を終了させると同時に、第2の工程を開始してリン化硼素緩衝層を形成すると、表面状態に優れるリン化硼素緩衝層を形成でき、しいては連続性に優れるリン化硼素系結晶層を形成するに効果を上げられる。

【0049】また、本発明に係わるリン化硼素緩衝層及びリン化硼素系結晶層とを用いてリン化硼素系半導体素子を構成すると、例えばpn接合特性に優れる高輝度のLEDを提供できる。

【図面の簡単な説明】

【図1】本発明の第3実施例に係るリン化硼素結晶層のX線回折パターンを示す図である。

【図2】本発明の第4実施例に係るLEDの平面模式図である。

【図3】図2に示すLEDの破線X-X'に沿った断面
模式図である。

【符号の説明】

1A エピタキシャル積層構造体

1B LED

101 珪素単結晶基板

102 リン化硼素緩衝層

103 n形リン化硼素結晶層

104 発光層

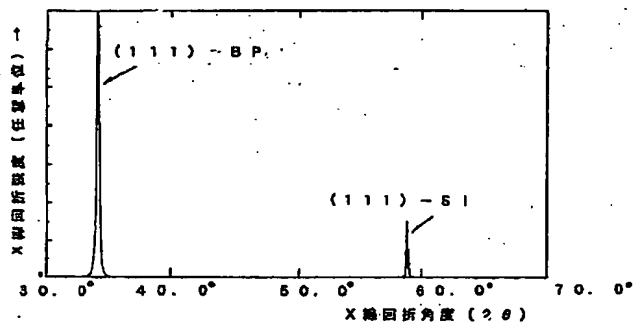
105 蒸発防止層

106 p形リン化硼素結晶層

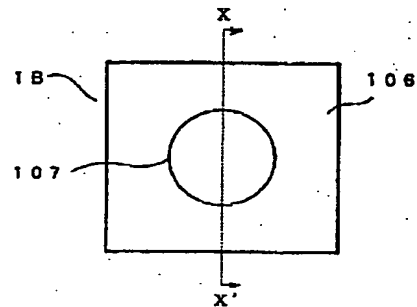
107 表面電極

108 裏面電極

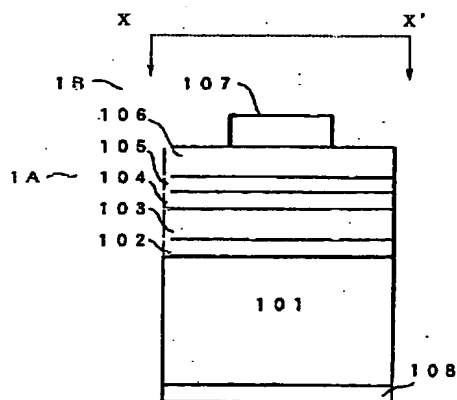
【図1】



【図2】



【図3】



フロントページの続き

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